Lead Mobility at Shooting Ranges

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at Shooting Ranges

Prepared for:

S A A M I
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Founded 1926

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Published by

Sporting Arms and Ammunition Manufacturers' Institute, Inc.
11 Mile Hill Road, Newtown, Connecticut 06470

Printed in the United States of America.

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GLOSSARY

The following are explained in layman's terms in the context in which they are used in this document. The reader is referred to a dictionary for a definition of these and other terms.

Adsorption/desorption - Adsorption is a process by which dissolved lead or other ions are chemically bound to the surface of particles in contact with the solution(e.g., clay particles in suspension in water). Desorption is the reverse of adsorption, and is the process by which adsorbed lead or other ions are released into solution. In natural waters adsorption and desorption both go on continuously, and factors such as pH determine which predominates.

Bioavailability - Presence in a chemical and physical form that can enter the physiological processes of organisms. Lead dissolved in water is bioavailable, while metallic lead is not. As lead changes forms (e.g., metallic lead oxidizes into lead compounds that are more soluble) its bioavailability changes. If metallic lead is ingested (e.g., by waterfowl) the portion that dissolves while passing through the digestive tract becomes bioavailable.

Cation Exchange Capacity - An easily measured property of soil that quantifies the amount of metal (positively charged) ions it can bind up.

Complexation - A process by which lead or other ions combine with dissolved substances (often large organic molecules), and thereby increase the amount of lead in solution.

Distribution coefficient (K_d) - The ratio of the amount of chemical in solid form to the amount dissolved in water under stable conditions. The higher the K_d, the less material can enter solution.

Eh - A measure of the oxidation condition (or oxidizing ability) of a mixture. Large positive values indicate highly oxidized conditions, while large negative values indicate highly reduced (anoxic) conditions.

Equilibrium - Stable conditions under which there is no net transformation of material from one form to another.

Geochemical - Chemical processes taking place in, or involving components of, soil or sediment.

Kinetic - Involving motion or time. Kinetic considerations deal with conditions at a point in time or during a finite time period, recognizing that conditions may be different at other times.

Mobility - In this document mobility refers to lead entering and remaining in solution in surface or ground water, and in the water trapped in the spaces between soil and sediment particles. It includes the dissolution of lead as well as processes that determine whether the lead remains in

solution.

Oxidation/reduction - Oxidation originally referred to combining with oxygen, as in iron combining with oxygen and oxidizing into iron oxide (rust). Chemically this involves the loss of electrons by the iron, and the term oxidation has evolved to refer to any process involving the loss of electrons, such as the conversion of metallic lead into lead ions. Reduction is the reverse of oxidation, or the gain of electrons, such as converting lead ions to metallic lead. Oxidation and reduction are usually described together as oxidation/reduction or redox processes.

pH - A standard scale for measuring acidity, on which values from 7 down to 0 are progressively more acidic and values from 7 to 14 are progressively more basic or alkaline. A pH of 7 is neutral. Most surface water is slightly acidic to slightly basic, and typically has a pH somewhere between about 5.5 and 8.0.

Precipitation/dissolution - Precipitation is a process in which dissolved constituents combine to form a relatively insoluble compound (e.g., dissolved lead and dissolved sulfate can combine to form the relatively insoluble precipitate lead sulfate). Dissolution is the reverse of this process in which solids dissolve as their individual soluble components. Site-specific conditions such as pH determine whether precipitation or dissolution will be the dominant process.

Thermodynamic stability - This is a chemical term referring to whether materials can transform or react chemically; it says nothing about the rate of transformation. Oxygen and nitrogen in air are thermodynamically unstable and will react with each other, although only very slowly. Metallic lead in shot or bullets at ranges is thermodynamically unstable and will form various lead compounds, although it may require many years to do so.

EXECUTIVE SUMMARY

Potentially adverse environmental impacts of lead associated with shooting ranges are receiving increasing attention. Lead poisoning of waterfowl and other migratory birds is a growing concern. A variety of issues have been raised about potential environmental impacts of lead associated with shooting ranges, including the potential mobility of lead that may be transported from shooting ranges. Of the metals present in shot and bullets, lead is the dominant component, is the most likely driver of potential environmental risk at shooting ranges, and will be the focus of this assessment. Hence, this review of scientific literature was conducted to summarize the current understanding of the environmental mobility of lead in surface or ground water, sediment, and soil, and the factors controlling lead mobility.

Lead Chemistry and Mobility

When bullets strike an impact berm they behave in a number of ways, including penetrating, agglomerating, fragmenting, smearing, and ricocheting. Most of the mass of lead in impact berms exists as intact bullets and relatively large fragments. But it is the very small particles of lead and the lead compounds resulting from the weathering of metallic lead that result in the most mobility. Furthermore, the continuous disturbance at some berms creates areas void of

vegetation, resulting in erosion during rainstorms. The associated surface water runoff can then be transported to adjacent water bodies and can under certain conditions can result in considerable transport of soil containing lead particles. Larger lead shot particles are not typically subjected to such physical processes, but are exposed to atmospheric conditions that result in transformation of metallic lead into more soluble forms.

The dissolution and mobility of lead derived from lead bullets and shot are ultimately dictated by a number of geochemical processes including oxidation/reduction, precipitation/dissolution, adsorption/desorption, and complexation/chelation. If metallic lead was inert in the environment, then it would not dissolve and would not be transported by any chemical means. However, metallic lead is not inert in the environment and is oxidized to more mobile forms. It is these subsequent oxidation products that determine the mobility of lead at shooting ranges and not the metallic lead itself. The rate of oxidation and the type of resultant oxidation products are highly variable and site specific.

Once oxidized, lead can be precipitated in a variety of forms including hydroxides, sulfates, sulfides, carbonates, and phosphates. Each of these precipitates are soluble, controlled largely by the site-specific water chemistry to which they are exposed. The important factors that directly control solubility are pH, oxidation-reduction (redox) conditions, and the concentration of the components that determine solubility (the primary solubility controls). As these parameters are

highly variable from one location to another, site-specific conditions determine how much lead can be solubilized. In general, lead is much more soluble under acidic (low pH) conditions than at neutral or alkaline (high pH) conditions, but this generality can be violated under a variety of situations. Some precipitates, especially phosphates and sulfides, are particularly effective at controlling lead solubility, often resulting in maintenance of very low lead concentrations in water. Additionally, factors controlling solubility can substantially reduce the bioavailability of lead in sediments and/or soils. The primary solubility control factors establish an upper limit on the amount of dissolved lead present in surface or ground water, and often keep lead concentrations below levels of concern.

Concentrations of dissolved lead in surface and ground water are also effectively controlled by adsorption processes. Lead can be adsorbed by a variety of materials including organic matter, iron and manganese oxyhydroxides, clays, carbonates, and sulfides. It is expected that lead mobility will be effectively controlled by adsorption under the majority of conditions found on shooting ranges. In general, neutral or slightly alkaline conditions will be expected to give rise to low mobility conditions and only acidic conditions will result in substantial mobility. However, there are several exceptions to this generality, as adsorption processes are extremely complex and highly dependent on site-specific conditions.

Complexation/chelation and transport of particulates that contain lead are complicating factors that may increase physical movement of lead. Particulate transport mechanisms may be effective in altering the distribution of lead over time but may not have a substantial effect on bioavailability.

Studies published to date indicate a general lack of lead mobility under most environmental conditions. From the relatively few lead mobility studies conducted at shooting ranges, pH appears to be an important factor. Surface water pH values of ≥ 7.0 tend to indicate restricted lead mobility whereas pH values of ≤ 6.5 tend to indicate enhanced lead mobility. Attempts to statistically correlate lead concentrations in water with pH, alkalinity, or shot density, however, have not been successful, likely due to complex interactions of several other environmental factors.

Management Options

If lead mobility needs to be controlled at a particular range, there are several potential options for effectively doing so. At some ranges, conditions will be such that control efforts will not be necessary. At other locations where control might be considered, site-specific conditions may favor some techniques over others. The mobility control techniques include recovery/recycling, control of storm water runoff, vegetative plantings, clay liners, lime addition, phosphate addition,

addition of other natural or synthetic chemical additives, and soil capping. Recovery and recycling may be the most cost-effective approach, although a combination of techniques may be required in some situations to effectively control lead mobility.

Geochemical principles and experimental results demonstrated that lead is present in the environment in a variety of chemical forms. Each form of lead has unique properties that affect dissolution and mobility. The interplay of these various forms determines solubility and thus mobility, bioavailability and toxicity. Measuring the total quantity of lead present in environmental media without other important parameters will yield an inaccurate picture of the dissolution and mobility of lead from a particular site. Because lead is readily precipitated and adsorbed, basing risk or cleanup decisions on total mass of lead alone will, in general, grossly overestimate risk, and result in unnecessary remediation efforts and unreasonable cleanup goals. This has occurred in the past and may occur in the future until more technically sound evaluative approachs are taken.

Analytical Considerations

A number of analytical procedures used to estimate lead mobility and bioavailability in environmental media can be misleading. The Toxicity Characteristic Leaching Procedure (TCLP) does not mimic realistic environmental conditions at shooting ranges, and is likely to

overestimate lead mobility at most shooting ranges. Existing state leaching procedures may be more or less stringent that TCLP depending on the extraction procedure employed. Simple measurements of lead concentrations in soil and sediment do not provide an accurate assessment of lead bioavailability or mobility. The simplest and most reliable indicator of lead mobility in surface water at existing or historical ranges is analysis of the water body in question. If detailed evaluation of mobility in groundwater is necessary, appropriate mathematical models may be useful.

1. INTRODUCTION

Public and regulatory concern about the potential effects of lead in the environment has increased dramatically over the last ten years. Potential risks associated with environmental and human exposure to lead in air, paint, drinking water, surface waters, soils and sediments are potentially significant, and shooting ranges are under increasing scrutiny.

In the context of this document "shooting ranges" refer to shotgun (trap, skeet, and sporting clays) ranges, and outdoor pistol and hand-held rifle ranges (both military and civilian), and the kinds of shooting and ammunition typical of such ranges. The term "ranges" refers specifically to areas where shot or bullets and associated fragments are found on the ground or in backstop berms. Even though hunting and other types of shooting are not addressed directly in this document, many of the factors and processes discussed also apply to spent ammunition generated by these activities.

Numerous issues have been raised about potential environmental impacts associated with shooting ranges. Lead has received the most attention, although other constituents in bullets, jackets, and shotgun pellets have been mentioned. Because lead is the overwhelmingly dominant component in bullets and shot and the subject of most attention, this document addresses the

environmental mobility of lead. Mobility in this document refers to lead entering and remaining in solution in surface or ground water, and in the interstitial spaces within soils and sediments. If metallic lead is transformed to dissolved phases, it is subject to potential transport and uptake by aquatic organisms, birds, mammals and humans. This document addresses the factors controlling lead mobility. The hydrodynamics of transport once lead is dissolved in the water are beyond the scope of this discussion, as are the potential exposure mechanisms and toxicological effects of lead ingested by animals or humans.

Ranges exist in a wide variety of environmental settings, and the site-specific hydrologic and geologic conditions can greatly influence lead mobility. The following illustrates some of these conditions, all of which can interact in complex ways:

- Water - At many ranges bullets or shot are deposited on land, but at some the lead falls directly into water.

- Rainfall - The amount and intensity of rainfall can greatly affect lead mobility.

- Acidity - The acidity of soil, rainfall and surface water are interrelated and can greatly influence mobility.

·   Vegetation - Vegetation affects runoff and erosion rates, as well as influencing the chemical characteristics of soil that determine mobility.

·   Soil - Characteristics such as mineralogy, coarseness, organic matter content and pH affect lead chemistry and mobility.

Given the amount of lead and the diversity of conditions influencing lead mobility, it is important to understand the primary mechanisms that determine the mobility of lead at outdoor shooting ranges. This literature review was undertaken to:

·   determine the major physical and chemical processes controlling the mobility of lead at outdoor shooting ranges,

·   identify options that might be useful in controlling lead mobility where appropriate, and

·   describe test procedures used to measure lead mobility.

Chapter 2 of this report provides a brief overview of the typical metallurgical composition of bullets and shot, and introduces some physical factors that influence lead mobility at ranges.

Chapter 3 presents a detailed discussion of the chemical processes and control mechanisms that determine lead mobility in the environment. Chapter 4 identifies several possible options for managing mobility at ranges based on the findings of Chapter 3. Chapter 5 discusses some of the strengths, limitations, and appropriate uses of several test procedures used by investigators and regulators to measure lead mobility. Chapter 6 presents the conclusions and recommendations from this study.

2. FATE AND TRANSPORT OF LEAD AT SHOOTING RANGES

2.1 COMPOSITION OF BULLETS AND SHOT

Metallic lead is deposited on shooting ranges in one of two primary ways; either as lead shot fired at airborne targets, or as bullets fired into impact berms. Relatively small amounts of lead may also come from vaporization of lead from the heat of burning powder and barrel friction, and from lead compounds in primers. This is a small amount of lead relative to bullets and shot, and is probably affected by the same chemical processes. Therefore, this lead is not addressed seperately in this document. Lead is more than 90 percent of the mass of shot used in trap, skeet, sporting clays and similar shotgun sports (New York State Dept. Env. Conserv. 1993). Ammunition fired at small-arms ranges at U.S. military installations typically consists of a bullet, a cartridge case that contains the propellant, and an ignition system or primer (Heath et al. 1991). The bullet composition is mostly lead, with antimony added to the lead for hardness. Composition of bullet cores is typically in the range of 90 to 99% lead plus 1 to 10.5% antimony and 0.1% copper (Heath et al. 1991).

2.2   FATE OF BULLETS IN IMPACT BERMS

Impact berms at shooting ranges are designed to capture fired ammunition. Previous studies have indicated a bullet-to-soils content of up to 30% by volume in impact berms at some military small arms ranges (Karr et al. 1990a; Heath et al. 1991). After extended periods of use, the berms may become saturated with bullets, resulting in possible ricochet of fired bullets off of other bullets in the berm and into surrounding areas (Karr et al. 1990b). The continuous disturbance by bullets entering the berm can also create areas that are void of vegetation. Steep-sided berms without vegetation are particularly susceptible to erosion during rainstorms and the associated surface water runoff can be quickly transported to adjacent water bodies (Karr et al. 1990a; Heath et al. 1991). This can result in considerable transport of lead particles from berms under certain conditions.

When bullets hit a berm they may behave in any of several ways, including:

- Penetrating - Sporting loads typically expand and do not penetrate as deeply as full jacketed bullets from military loads.

- Agglomerating - The impact of one bullet on another may join them into a single mass, especially if the bullets are of relatively soft composition.

- Fragmenting - Bullets may strike stones or other bullets already in the berm and fragment into large or small pieces, even to microscopically fine particles.

- Smearing - Bullets penetrating the berm may leave a smear of extremely fine lead on the surface of soil particles they contact.

- Ricocheting - Bullets may strike other bullets already in the berm and ricochet into surrounding areas.

Most of the mass of lead in impact berms exists as intact bullets and relatively large fragments, but lead is also present in other forms including smears, fine particles, and weathered products (Novstrup et al. 1992; Johnson et al. 1993). As a bullet penetrates a berm it may "smear" on contacted soil particles or on wooden components of the berm structure where they are penetrated by bullets. Johnson et al. (1993) hypothesized that when bullets penetrate at high velocity, friction produces temperatures sufficient to promote smearing of lead on surfaces the bullet contacts. The hypothesized process is somewhat analogous to marking on paper with a pencil. Ultra fine lead particles (approximately 5 microns) were also found in berms, likely as a result of dust-sized lead fragments being produced during impact with the berm (Johnson et al. 1993). These microparticulate forms of lead in impact berms can have considerable implications regarding lead mobility and potential management options at small-arms ranges.

2.3   FATE OF SHOT AT SHOOTING RANGES

Shot fired at trap, skeet and sporting clays ranges falls to the ground in a reasonably defined area usually several acres in size. Lead shot hitting clay targets may flatten, fragment or ricochet before reaching the ground. Otherwise, lead shot remains intact upon reaching the surface of soil or aquatic sediments until physically transported (Section 2.4) or chemically transformed (Section 3).

2.4   PHYSICAL TRANSPORT OF LEAD AT SHOOTING RANGES

Sever (1993) presented several mechanisms by which lead can be transported at shooting ranges, including:

- Dissolved in storm runoff - Lead shot or bullet fragments in the field may weather through time into more water-soluble compounds (Section 3) and subsequently be transported into surface waters. Factors influencing the amount of dissolved lead in storm water runoff may include annual precipitation rate, pH of rain and surface water, contact time, soil cover, and forms of lead present.

- Lead particles or lead on soil particles in storm runoff - Lead present as shot or bullet fragments may be physically transported by storm runoff into surface waters. This pathway is dependent on rainfall intensity, topographic slope, soil type, velocity of runoff, and presence of vegetative cover or man-made structures. Lead fragments are dense and would not be as subject to transport by runoff as would lead sorbed to soil particles.

- Dissolved in ground water - Water-soluble forms of lead may be transported to groundwater under certain conditions that may be found at some ranges and can be influenced by annual precipitation rate, soil type, soil chemistry, depth to groundwater, and pH of groundwater.

- Wind-driven lead dust or lead associated with wind driven soil particles - Airborne lead dust occurs during the firing process and upon bullet impact with a berm, where dust production is influenced by bullet construction and velocity, soil type and soil moisture.

2.5 EVALUATION OF LEAD IN THE ENVIRONMENT

Some of the major criteria and guidelines established at the federal level for lead in water and soil are presented below; some state standards are more stringent than these U.S. Environmental

Protection Agency (EPA) values. This is not an exhaustive list, and these values are presented merely for information as an indication of the concentrations that might be appplied to lead at shooting ranges in a regulatory context.

WATER

Aquatic Life Criteria (60 Fed Reg 22228; 4 May 1995)

- Freshwater Chronic Criteria (dissolved) 1.0, 2.5 and 6.1 μg/L (parts per billion - ppb) at water hardnesses of 50, 100 and 200 mg/L, respectively.

- Saltwater Chronic Criteria (dissolved): 8.1 μg/L

Drinking Water Regulation Values (40 CFR 141)

- Maximum Contaminant Level Goal (MCLG): zero [40 CFR 141.51]

- Lead "Action Level": 15 μg/L in >10 % of tap water samples [40 CFR 141.80]

SOIL

<u>RCRA Hazardous Waste Characterization (40 CFR 261.24)</u>

- TCLP leachate extract concentration of 5 mg/L (parts per million - ppm)

<u>Residential Screening Level for Soils (U.S. EPA's OSWER Directive # 9355.4-12)</u>

- Recommended screening level for soils for residential land use: 400-5,000 mg/kg

  (ppm) depending on site conditions, with remediation where concentrations

  exceed 5,000 ppm.

  This screening value is not a cleanup goal.

3. CHEMICAL PROCESSES CONTROLLING THE FATE AND TRANSPORT
    OF LEAD

3.1 OVERVIEW

Geochemical interactions are possibly the most important processes in understanding lead

solubility and mobility in the environment. As a result, this chapter describes the role of the

important geochemical processes influencing the fate and transport of lead. The information

provided ranges from non-technical descriptions of the basic chemical processes, to a highly

specific and technical treatment of the published literature. Geochemistry is extremely complex

and attempts at simplifying it are difficult at best. The technical review is not a complete treatise

on the topic, but rather a strong foundation for technical staff who must conduct site-specific lead

studies.

Section 3.2 presents a brief overview of the four important processes controlling lead fate and

transport. Within Section 3.2, each of these four processes are discussed separately and each of

these four processes are subdivided into five sections.

- First, each process and important terms are defined for those unfamiliar with the

    terminology used.

- Second, the environmental significance of each process is described.

- Third, a description of the important factors influencing the chemical process is summarized.

- Fourth, the bulk of the geochemistry, including a detailed review of pertinent scientific literature is provided. This section is technical in nature.

- Fifth, a summary is presented where the process is put into perspective with respect to shooting ranges.

Section 3.3 reviews some modeling approaches that have been used at lead contaminated sites. These approaches are of interest because they have been employed to address issues of lead fate, transport, and bioavailability for Resource Conservation and Recovery Act (RCRA) and Comprehensive Environmental Response and Compliance Liability Act (CERCLA) designated facilities throughout the country. The articles discussed are all relatively recent and represent state-of-the-art approaches for estimating lead fate and transport.

Section 3.4 briefly summarizes the few published field studies of lead mobility at outdoor shooting ranges.

Lastly, Section 3.5 provides a summary of the geochemical studies discussed and attempts to put this information into the context of a shooting range.

3.2 GEOCHEMICAL PROCESSES AND FACTORS CONTROLLING THE FATE AND TRANSPORT OF LEAD

The fate and transport of lead derived from lead shot is dictated by a number of geochemical processes including:

- oxidation/reduction - the process responsible for converting metallic lead into more soluble forms, reduction being the opposite of oxidation.

- precipitation/dissolution - the process that removes lead from solution as a discrete solid form, dissolution being the opposite of precipitation.

- adsorption/desorption - the process through which naturally occurring mineral/organic remove lead from solution by binding them to their surfaces, desorption being the opposite of adsorption.

- complexation/chelation - the process where dissolved lead associates with other dissolved materials, resulting in higher dissolved lead levels.

Each of these processes are in turn influenced by a series of conditions present at any particular site such as pH, chemical constituents, soil or sediment characteristics, and the oxidation/reduction potential. A detailed description of each of these processes follows below.

3.2.1 Oxidation/Reduction Processes

3.2.1.1 Definition

Oxidation is the chemical process through which a chemical is converted from a reduced form to a more oxidized form. For example, in the case of lead (chemical symbol Pb), this process is responsible for the conversion of metallic lead Pb^0 to the more oxidized forms Pb^{2+} and Pb^{+4}. For metals, the more oxidized forms are generally more soluble. Reduction is the reverse of this process and is responsible for converting Pb^{4+} to Pb^{2+} and Pb^{2+} to Pb^0. These two separate processes are generally described together as oxidation/reduction or redox processes.

3.2.1.2 Environmental Significance of Oxidation/Reduction Processes

Oxidation/reduction processes are important because they determine which oxidation state of lead will dominate under any particular set of conditions. The prevalence of one oxidation state of lead over another determines, in part, what chemical forms of lead will be present at a particular site. This in turn determines the potential for mobility and the potential for environmental effects.

3.2.1.3 Factors Affecting Oxidation/Reduction Processes

The oxidation/reduction conditions found in the environment are affected by a variety of chemicals present in soil, sediment, or water. These factors include dissolved oxygen levels, whether soil is saturated with water (flooded), proximity to the surface, infiltration rate, organic carbon content, and biological activity. Oxidation/reduction conditions can vary dramatically and can be estimated from site-specific observations or determined analytically through a variety of techniques, including direct Eh measurements. Eh is a measure of the electrochemical potential relative to the standard hydrogen reference electrode and is reported in volts.

3.2.1.4 Chemistry of Oxidation/Reduction Processes

Metallic lead (Pb^0) is insoluble in water and if it did not undergo chemical transformations would not be dissolved and subsequently mobilized by surface or ground water (Garrels and Christ 1965). Metallic lead is, however, thermodynamically unstable in the geochemical environment present on most shooting ranges. In this context, the term unstable means that metallic lead will ultimately be transformed to other more stable forms depending on the environment. A more familiar example of this is nitrogen and oxygen in air. Air is predicted to be a thermodynamically unstable mixture and nitrogen and oxygen will ultimately combine to form nitrogen oxides. This process occurs only very slowly. While many of these processes are relatively slow they none-the-less do occur over time. These processes are best illustrated by an examination of the geochemical stability field diagram for lead in pure water (Figure 3.1, which has been slightly modified from Hem (1976a). Note that metallic lead (Pb) is stable in only a very small fraction of the diagram. Typical groundwater and surface water conditions occupy only a fraction of the total range of pH (5-9). As a result, the conditions under which metallic lead would be predicted to be stable in the natural environment are relativeely uncommon. This implies that metallic lead will likely be converted into other oxidized forms in most natural environments. Further, Figure 3-1 does not include the carbonates, sulfates, sulfides, and phosphates, and as a result exaggerates the range over which metallic lead would be stable in the environment (Garrels and Christ 1965; Hem 1976a; Rai et al. 1984).
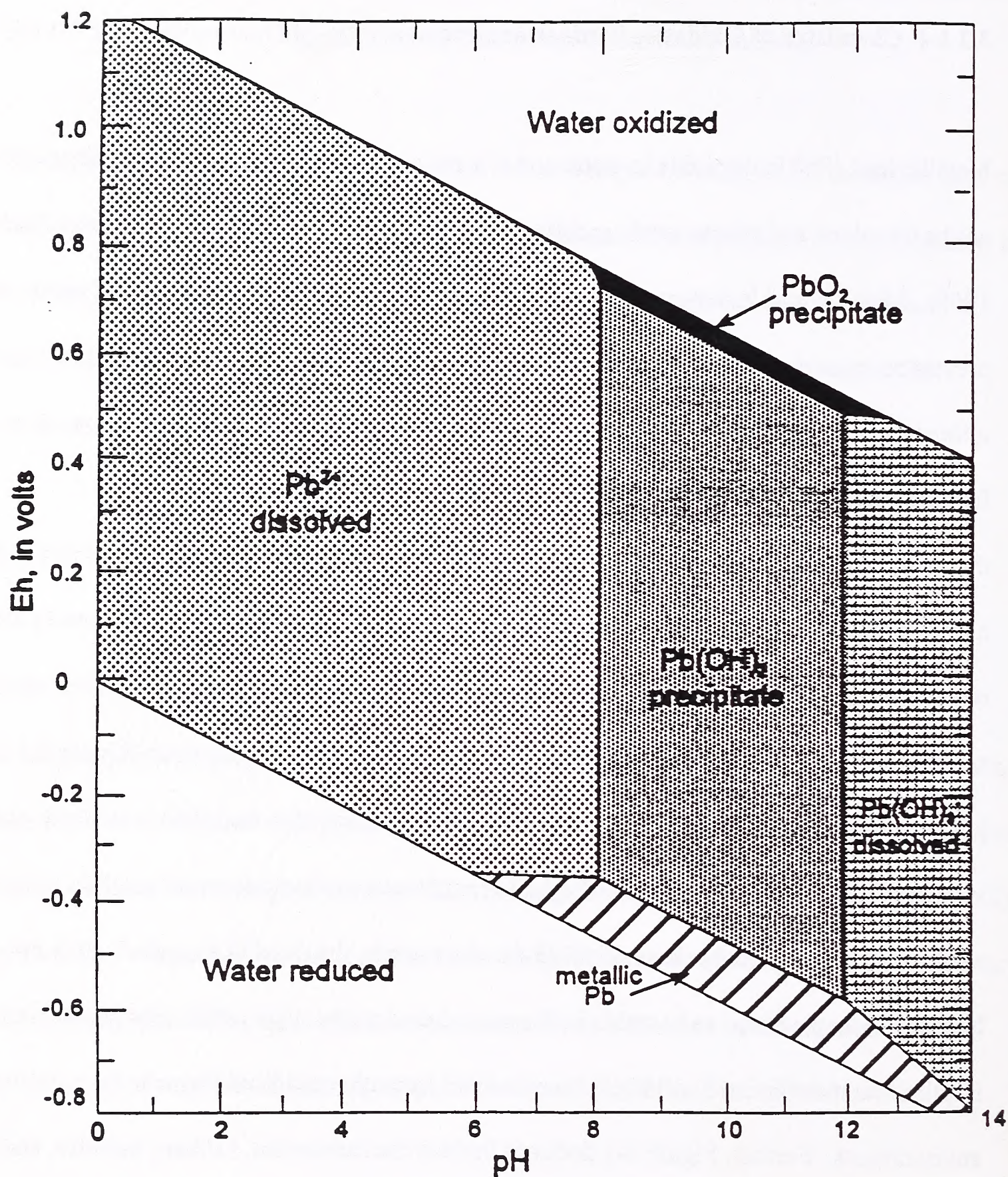
Figure 3-1. Equilibrium stability field diagram for solids and dominant solute species in a lead-water system as functions of pH and Eh (reduction/oxidation potential). Diagram shows which species are likely to exist at various Eh and pH conditions when dissolved lead activity = $10^{-8.32}$ mol/l at 25°C and 1 atm pressure.

The thermodynamic instability of metallic lead implies that it will ultimately be converted to more soluble forms, but does not indicate how fast that process will occur. It is clear that lead shot visibly oxidizes once released into the environment. It is expected that the dissolution and corrosion rates will be site specific and may vary substantially even within any specific site. This rate will change as a function of chemical parameters such as oxidation/reduction potential, pH, ionic strength, concentration of specific oxidizing agents (such as dissolved or pore oxygen), and other species with which lead will react to form precipitates. The presence of reactants (e.g., acids, bases, sulfate, carbonate) in general will lead to faster corrosion rates. Select chemical species may actually inhibit the oxidation of lead by forming a protective and non-reactive layer that retards contact between the remaining metallic lead and other reactants (e.g., phosphate is used to inhibit the corrosion of iron).

Jorgensen and Willems (1987) report that the lead pellets collected for their chemical studies were corroded and partially covered by white, grey, or brown material. They also estimated that half of the metallic lead would be transformed in 40-70 years, and completely transformed in 100-300 years. Bullets observed by staff from EA Engineering, Science, and Technology on World War I and World War II era shooting ranges evidence highly variable amounts of corrosion. Some of these bullets are found to contain little metallic lead and are instead filled with white, yellowish, brownish, or grey material. Others are much more intact and contain a significant portion of the original metallic lead. These observations suggest lifetimes for lead in

bullets on the order of 50-200 years, which is consistent with Van Bon and Boersema (1988) who report that lead shot dissolves at a rate of approximately 1% per year. Civil war bullets have been known to exist for 130 years with as much as 95% of the material intact. Battelle (1987) estimated that only 2% of lead at Lordship was lost in 50 years.

A number of physical processes will also affect the dissolution/corrosion rate. The ratio of surface area to mass is important and large bullets are expected to corrode at a substantially reduced rate compared to much smaller shot. Likewise, small particles of metallic lead that are abraded as bullets pass through soil are likely to degrade faster due to their high surface area/mass ratio. The infiltration of surface water into soil is expected to carry dissolved oxygen and lower pH water (particularly in acid rain depositional area). Higher infiltration rates and lower pH are both likely to increase corrosion rates. Depth of burial is likewise expected to affect the corrosion rate, at least in part by controlling the transpiration of soil oxygen (Jorgensen and Willems 1987).

3.2.1.5 Summary of Oxidation/Reduction Processes

Oxidation/reduction processes slowly corrode lead shot in the environment. The rate of corrosion has been estimated in only a few cases and has been reported as approximately 0.3 to 1 percent per year (Jorgensen and Willems 1987). Oxidation rates are generally expected to be

faster under higher infiltration rates, acidic or alkaline pH as opposed to neutral pH, or any other conditions that would increase the transportation of oxygen or other reactive chemicals to metallic lead. Lead that is oxidized is expected to be more soluble and thus more mobile than metallic lead.

3.2.2   Precipitation/Dissolution Processes

3.2.2.1 Definition

Precipitation is defined as a chemical process through which components that are dissolved in a solution combine to form a solid and drop out of solution. The definition further implies that the solid formed will be of a fixed composition. For example, calcium and sulfate combine to form a precipitate calcium sulfate (gypsum). The amount of precipitation/dissolution is determined by a thermodynamic constant known as the solubility product K_{sp}. For gypsum, the relationship is given by:

$$K_{sp} = [Ca^{2+}][SO_4^{2-}]$$

where:

$[Ca^{2+}]$	is the concentration of dissolved calcium
$[SO_4^{2-}]$	is the concentration of dissolved sulfate
K_{sp}	solubility product (a constant).

This equation gives the equilibrium solubility relationship. Dissolution is the opposite of precipitation in that it is the process by which solids are separated into their individual soluble components. The term solubility control generally refers to a solid that controls the dissolved concentration of the component of interest. For example, calcium sulfate (gypsum) determines how much calcium and sulfate will be present in water in contact with it. Likewise, the presence of calcium sulfate and dissolved sulfate will determine the level of dissolved calcium. In this case, both calcium sulfate and dissolved sulfate can be referred to as solubility controls.

3.2.2.2 Environmental Significance of Precipitation/Dissolution Processes

Precipitation/dissolution processes, in part, determine the concentrations of materials ultimately encountered in environmental media. As dissolved metals are considered to be more mobile and more bioavailable than precipitates, it is important to understand what form of lead is present in order to accurately judge the potential for impact. A variety of lead compounds are known to form in the environment and their precipitation and/or dissolution largely determine dissolved concentrations in waters in contact with lead on shooting ranges.

3.2.2.3 Factors Affecting Precipitation/Dissolution Processes

Numerous factors affect the solubility of lead in the environment. The dominant factors affecting solubility of lead include pH, Eh, and the concentration of carbonate, sulfate, sulfide, phosphate and chloride. These factors interact in a complex fashion and their interplay determines the ultimate solubility of lead at a particular site. A number of geochemical speciation models have been devised to aid in the study of such complex systems and can produce reasonable estimates of solubility if the appropriate input variables are used. An examination of the important solids and solubility controls follows.

3.2.2.4 Chemistry of Precipitation/Dissolution Processes

A solubility control is defined as a solid phase whose presence determines the maximum dissolved concentration of a species in equilibrium with that solid. Solubility controls are useful in that they establish a practical upper limit to the dissolved concentration of a chemical of concern in water. In fact, some solids are so effective as solubility controls that they can be effectively exploited to manage lead mobility (see Chapter 4). For this reason, the discussion of the geochemistry of lead begins with a section that describes the potential solubility controls in some detail.

This process is distinct from adsorption in that the specified mineral (solid) phase contains the element of interest as an integral component. The solubility of any species, such as Pb^{2+}, is determined from the corresponding K_{sp} and the concentration of each of the other components of the particular solubility control. For example, if $PbSO_4$ is present as a solid phase in contact with water, then the concentration of Pb^{2+} would be given by the relationship $K_{sp} = [Pb^{2+}][SO_4^{2-}]$, where the solubility product (K_{sp}) is a constant (Garrels and Christ 1965; Hem 1976a; Rai et al. 1984).

A variety of lead-containing minerals are likely to precipitate under conditions present at or near shooting ranges. These minerals include lead oxides, hydroxides, carbonates, sulfates, sulfides, and phosphates (Jorgensen and Willems 1987; Hem 1976a; Rai et al. 1984). It is likely that one or more of these precipitated solids will be present at a given shooting range and will provide some measure of protection from dissolved lead mobility. The likelihood that any one of these mineral phases will be the primary solubility control depends on the solubility of the mineral and the concentration of each of its components in associated pore or surface water. As a result, the presence or absence of solubility controls is very site-specific.

The general conditions under which each of these mineral phases are likely to be important are discussed below. Additionally, the likely dissolved concentration of lead in contact with each of these phases will be discussed. It should be emphasized that it is difficult to identify primary

solubility controls that are present in small amounts or in amorphous forms. This has been

accomplished in only a few select cases involving lead shot (Jorgensen and Willems 1987). U.S.

EPA distributes their own geochemical speciation model (MINTEQA2) that can be used to help

address issues discussed in this section and was employed as a source of data for many of the

figures provided in this section (U.S. EPA 1990).

MINTEQA2 can be used to estimate the solubility of lead, given reasonable estimates of the

controlling parameters, and can be applied on a site-specific basis by a geochemist. MINTEQA2

can be applied in a tiered fashion and at relatively low cost for an initial screening assessment.

More detailed chemical information can be collected should more precise estimates of solubility

and identification of solubility controls prove necessary.

3.2.2.4.1 Lead Oxides and Hydroxides

Lead oxides are potentially the first products resulting from the direct oxidation of metallic lead

by oxygen. While oxides are potential initial products, they are not likely to exist for long

periods in the environment and should rapidly react with water to form lead hydroxide $Pb(OH)_2$

or other chemical constituents. Figure 3-1 is a thermodynamic stability field diagram showing

the relationship of lead hydroxides and oxides as a function of pH and Eh in pure water (adapted

from Hem 1976a). This diagram is overly simplistic and is used for illustrative purposes only.

Several components of typical surface and groundwater are not included and these components would significantly alter this diagram.

A diagram showing the solubility of lead hydroxide as a function of pH in distilled water as predicted by MINTEQA2 is presented in Figure 3-2. As indicated by the CO_2 free case (no air present) presented in this figure, lead hydroxide will effectively limit the solubility of lead in pure water to levels below 0.05 ppm at pH values in excess of 7.5. The majority of surface and ground waters have pHs below 8.5 (Garrels and Christ 1965). Although this curve is not representative of natural conditions, it does provide one bound for expected results.

A number of additional chemical species present in natural waters have the ability to affect the solubility of lead hydroxide. In particular, at pH values above 8.5 lead will complex with dissolved carbonate, resulting in higher dissolved lead concentrations. The amount of increase will change substantially depending on whether a fixed amount of carbonate is available or if the solution is in equilibrium with air or soil CO_2 levels. Figure 3-2 compares MINTEQA2 predictions when CO_2 is absent, when the partial pressure of CO_2 (P_{CO2}) was fixed at atmospheric levels (0.00034 atm), and when P_{CO2} was fixed at 10 times atmospheric levels. The latter case is more representative of CO_2 levels in sediment/soil pore gases. Note that as carbonate levels increase, the solubility of lead increases at pHs above 7. What this effectively means is that lead hydroxide is less effective at controlling dissolved lead when carbonate is present. At high
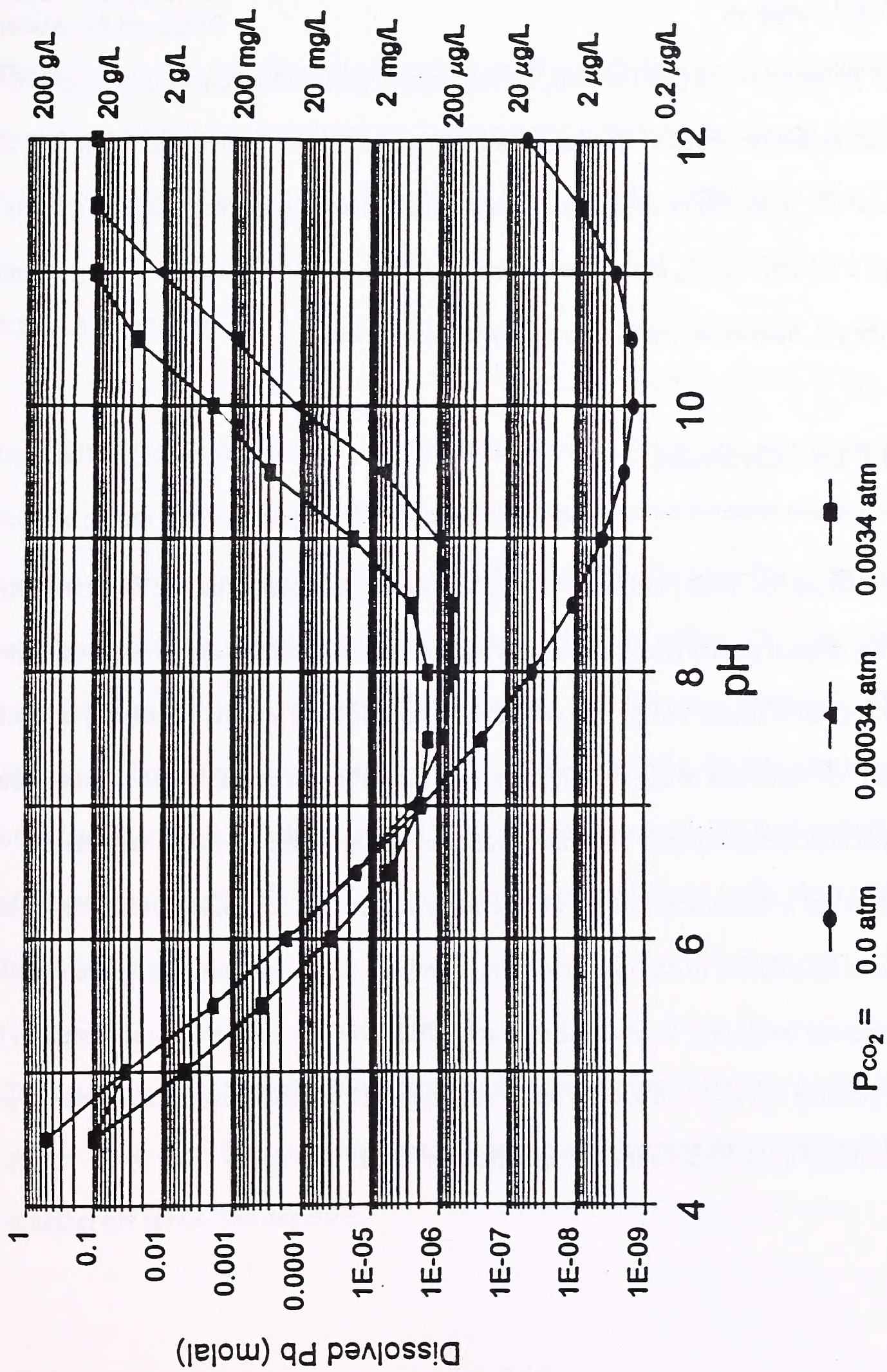
Figure 3-2. MINTEQA2 predictions of lead solubility as a function of pH and PCO_2. Each curve provides the predicted dissolved lead level as a function of pH, at the specified partial pressure of CO_2.

P_{CO_2} = 0.0 atm   0.00034 atm   0.00034 atm   0.0034 atm

enough carbonate levels (0.0034 atm), the solubility control shifts from lead hydroxide to lead carbonate as demonstrated by the downward shift of the curve relative to the lower CO_2 cases at pHs below 7. It should be emphasized that alkaline water with low carbonate levels will undergo a pH shift as CO_2 is absorbed from air. As CO_2 dissolves in alkaline water it tends to lower the pH, thereby decreasing the ability to dissolve lead.

3.2.2.4.2 Lead Carbonates

Lead carbonate (cerussite) and lead hydroxyl carbonate (hydrocerussite) are both naturally occurring mineral phases (Hem 1976a) and are potential solubility controls on shooting ranges (Jorgensen and Willems 1987). The solubility of both of these minerals is directly controlled by the dissolved carbonate concentration; the higher the carbonate concentration the lower the dissolved lead concentration. The concentration of the carbonate species in water is pH dependent and is the most prevalent species under alkaline pH conditions. At neutral to acidic conditions bicarbonate or carbonic acid forms dominate. A further complication to the picture is that carbonate levels may be established at some fixed total amount in a closed system or by the partial pressure of P_{CO2} in an open system. Any approach to estimating the maximum level of lead solubility must consider the site specific conditions.

The formation of hydrocerussite is dependent on pH directly because it also contains hydroxyl groups. As a result, hydrocerussite would be expected to become the primary solubility control at higher pH levels than cerussite (Hem 1976a; Rai et al. 1984; Garrels and Christ 1965).

3.2.2.4.3 Lead Sulfates

Lead sulfate (anglesite) and lead hydroxyl sulfate (hydroanglesite) are naturally occurring mineral phases common in a number of mineral deposits and are potential primary solubility controls on shooting ranges (Jorgensen and Willems 1987). The solubility of both of these minerals is inversely related to the concentration of dissolved sulfate. The concentration of the sulfate species in water is generally pH independent. This is because protonation of dissolved sulfate does not occur except at extremely low pH levels (pH<2). On the other hand, a number of sulfate minerals (e.g., calcium sulfate (gypsum)) are common in the environment and may be effective in altering the dissolved sulfate levels (Garrels and Christ 1965; Hem 1976a; Rai et al. 1984).

The formation of hydroanglesite is also dependent on pH directly because it contains hydroxyl groups. As a result, hydroangelsite would be expected to become the primary solubility control at higher pH levels than anglesite.

3.2.2.4.4 Lead Sulfide

Lead sulfide (galena) is an important solubility control of lead in the environment and is relatively common. This mineral is not stable in oxidizing, near surface conditions and will transform into those minerals that are thermodynamically preferred in oxidizing conditions (e.g. angelsite, cerussite). In ore deposits where galena has been exposed to oxidizing groundwaters for long periods of time, it is often tranformed into the anglesites and cerussites previously discussed. These anglesites and cerussites commonly form coatings (druzes) on the underlying galena and can totally replace the galena (Sinkankas 1964).

Lead sulfide's $K_{sp} = 10^{-33.4}$ which indicates that it is very insoluble (Casas and Crecelius 1994; DiToro et al. 1990). The factor that determines the likelihood of lead sulfide as a primary solubility control is the presence of sulfide. Sulfide is very unstable except under reducing conditions such as those found in sediments or flooded soils with a high organic content and will be transformed to sulfate in more oxic waters. It should be emphasized that lead sulfide can in many cases effectively limit dissolved lead to very low levels. Further, numerous studies have shown that the lack of bioavailability of lead is often directly correlated to sulfide levels and that lead sulfide is not very bioavailable to benthic organisms (Casas and Crecelius 1994; Burgoin et al. 1991a, 1991b). Because lead is so effectively bound by sulfides in sediments, simultaneously extracted metal/acid volatile sulfide ratios have been shown to accurately reflect the potential

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toxicity of lead in sediments to benthic communities, with ratios less than 1.0 generally showing

no toxicity (Casas and Crecelius 1994; Burgoin et al. 1991a, 1991b).

3.2.2.4.5 Combined Picture

In summary, dissolved lead concentrations will be affected by a number of factors present in the

environment. Of these, pH, Eh, carbonate, and sulfur are the commonly occurring factors that

are likely to have the greatest effect. The overall Eh-pH stability field diagram that results when

the total aqueous species of carbonate and sulfur are each assumed to be millimolar (modified

slightly from Hem 1976a), is presented in Figure 3-3.

As shown in Figure 3-3, $Pb(OH)_2$ is predicted to be the dominant solubility control at pHs

exceeding 8.5. At pHs between 7.8 and 8.5, $Pb_3(OH)_2(CO_3)_2$ is predicted to be the solubility

control and at pHs from 5.3 to 7.8 $PbCO_3$ is expected to dominate. At pHs below 5.3, $PbSO_4$ is

expected to be the solubility control. The vertical lines represent the expected dissolved lead

concentrations in equilibrium with these solids under these conditions. Note that this diagram

can change considerably as a result of actual site-specific carbonate, sulfate, lead, pH levels, and

Eh potentials. This figure provides an illustrative example of the factors that might be present in

the environment and provides a crude estimate of when different solubility factors may play a
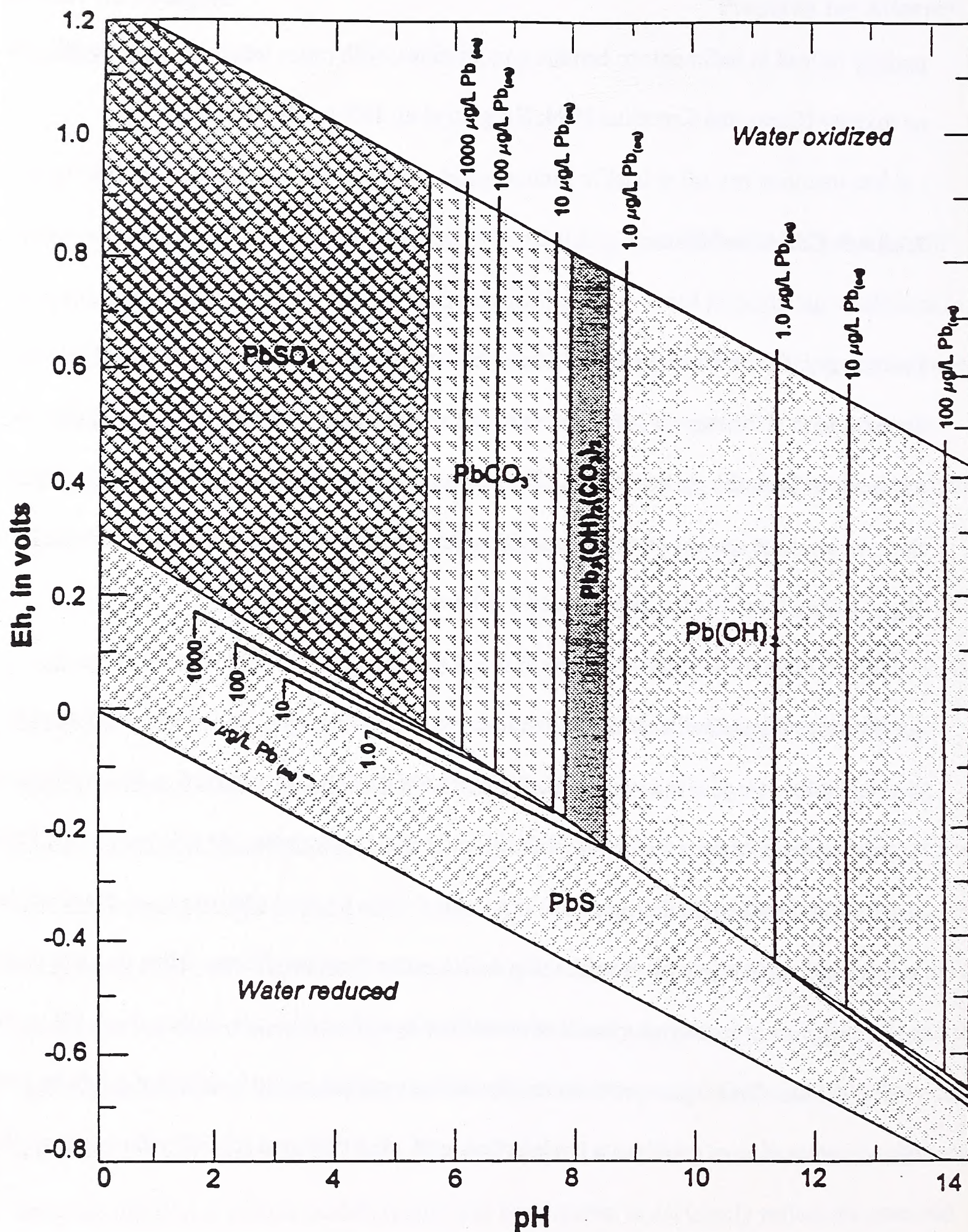
Figure 3-3. Equilibrium stability field diagram for solids and dominant solute species in a lead-water system Pb+CO₂+S+H₂O at 25°C and 1 atm pressure. Diagram shows which species are likely to form as a function of pH and Eh when ionic strength = 0.005. (Total dissolved CO₂ = 0.001 molar) (Total dissolved S = 0.001 molar)

critical role. Table 3-1 contains the thermodynamic formation constants reported by Hem

(1976a) that were used in the construction of the stability field diagram presented in Figure 3-3.

It is also possible to use a geochemical speciation model such as MINTEQA2 (U.S. EPA, 1990a)

as an aid to estimating solubilities. Consider an example where water in soil contaminated with

lead (vadose zone) mixes with other water (aquifer) that contains sulfate and carbonate. In this

case, we assume the total starting carbonate content is 1.0 m molar, total sulfate is 1.0 m molar,

and total lead is 0.1 m molar after mixing occurs. The difference from the stability diagram

presented above is that the concentrations of carbonate, sulfate, and lead are input as starting

totals and the total equilibrium dissolved levels are not fixed. MINTEQA2 provides a prediction

of how much and what kind of lead precipitates would be expected to form under these

conditions. The dissolved levels of lead and the corresponding solid precipitates of lead are

presented in Figure 3-4. Note that this diagram is similar to the predictions provided in Figure 3-

3. Lead sulfate is expected to form at low pH, lead carbonate at intermediate pH, and lead

hydroxide at elevated pH. Lead hydroxyl carbonate is absent from the picture in this particular

case; however, it was predicted to be only slightly undersaturated at the boundary between lead

carbonate and lead hydroxide.

Hem (1976a) compared a number of dissolved lead concentrations to conditions present (or

assumed present) in the environment and showed that solubility controls alone generally

TABLE 3-1 Standard Gibbs free energies of formation of lead species and related solutes. [c, solid state; aq, dissolved] from Hem (1976a)

FORMULA	FREE ENERGIES
Pb^{-2} (aq)	-5.83
$PbOH^-$ (aq)	-51.41[1]
$Pb(OH)_2$ (aq)	-95.8
$Pb(OH)_3^-$ (aq)	-137.6
$Pb_4(OH)_4^-$ (aq)	-225.6[1]
$PbCl^-$ (aq)	-39.39
$PbCl^2$ (aq)	-71.03
$PbSO_4$ (aq)	-187.38
PbO (c)[2]	-44.91
PbO (c)[3]	-45.16
$Pb(OH)_2$ (c)	-108.1
PbS (c)	-22.96
$PbCO_3$ (c)	-150.3
$Pb_3(OH)_2(CO_3)_2$ (c)	-409.1
$PbSO4$ (c)	-194.36
PbO_2 (c)	-51.95
Pb_3O_4 (c)	-143.7
H_2O[4]	-56.69
OH^- (aq)	-37.59
H_2S (aq)	-6.66
HS^- (aq)	2.88
$SO4^{-2}$ (aq)	-177.97
HSO_4^- (aq)	-180.69
H_2CO_3 (aq)	-148.94
HCO_3^- (aq)	-140.26
CO_3^{-2} (aq)	-126.17

Footnotes: [1] at 20°   [2] yellow   [3] red   [4] liquid
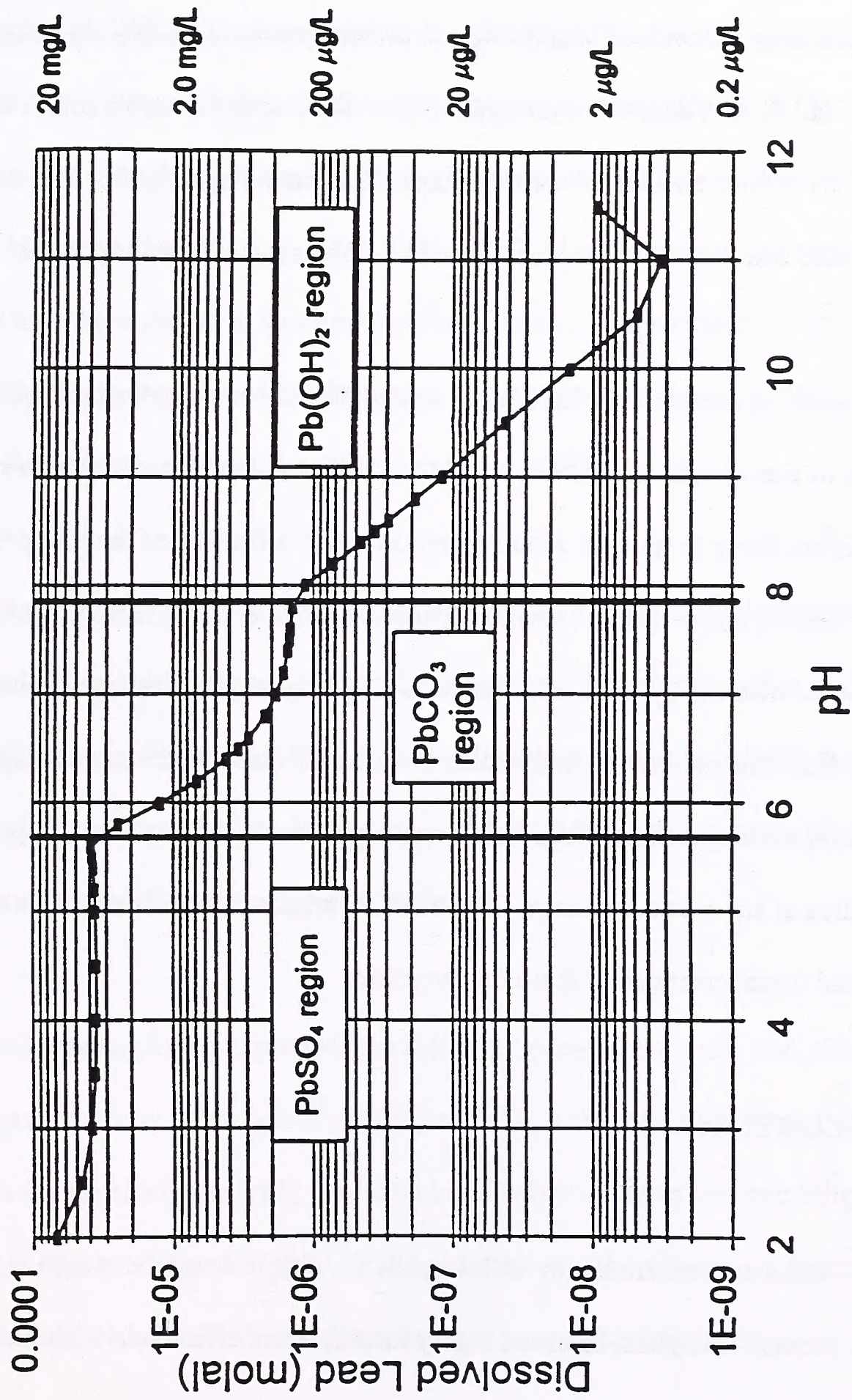
Figure 3-4. MINTEQA2 predictions of lead solubility controls as a function of pH. Line represents dissolved lead concentrations. At pH <5.7, PbSO$_4$ is present; at pH 5.7 - 7.8, PbCO$_3$ is present; at pH >7.8, Pb(OH)$_2$ is present. Total Sulfur = 0.001 M, Total Carbonate = 0.001 M, Total Lead = 0.0001M.

provided conservative (overestimated) dissolved lead concentrations. This is expected since other factors control dissolved lead levels and solubility controls define a maximum concentration. Further support of the applicability of solubility controls comes from Lund et al. (1991). They studied an alkaline wetland ecosystem containing lead shot in Western Australia and concluded that lead was not soluble or mobile under the conditions present.

While the analysis presented in this section cannot directly estimate lead solubility at shooting ranges due to site-specific interaction of many variables, it does illustrate that a number of lead precipitates are likely to form on shooting ranges. Only a fraction of the lead present on shooting ranges is likely to be present in a potentially mobile form. Further, these potentially mobile forms coupled with site-specific characteristics are likely to establish upper solubility limits, and thus act to limit the mobility of lead in dissolved forms. Because the controlling parameters vary substantially, a site-specific evaluation is necessary to accurately estimate the potential for lead solubilization at any particular range. However, accurate estimates may not be necessary if site-specific lead management actions are implemented.

3.2.2.4.6 Lead Phosphates

Natural phosphate levels are highly variable, but have special significance in regard to lead solubility because lead phosphates are highly insoluble and effectively limit the solubility of lead

at very low levels under nearly all naturally occurring Eh and pH conditions. Various forms of

pyromorphite ($Pb_5(PO_4)_3Cl$) where chloride is replaced by hydroxide or phosphate, are the lead

phosphates that are most likely to be formed in the environment (Harter 1979). Several studies

have shown that phosphates not only effectively control the solubilty of lead but also greatly

reduce its bioavaiability (Ma et al. 1993, 1994, 1995). Lead contaminated soils treated with

phosphate have been shown to successfully pass Toxicity Characteristic Leaching Procedure

(TCLP) extractions, the test used to determine whether a solid waste is classified as hazardous

under the Resource Convervation and Recovery Act (RCRA).

While lead phosphates occur in the environment they do not generally dominate the speciation of

lead due to the low levels of phosphate in the environment relative to sulfate and carbonate.

Santillan-Medrano and Jurinak (1975) discuss using batch studies to identify the solubility

controls and show that carbonate, hydroxide, and phosphate appear to be applicable solubility

controls in a variety of loams at different pH levels.

MINTEQA2 was employed to produce the solubility curves for several lead phosphate mineral

phases in pure water as a function of pH (Figure 3-5). It becomes clear from this figure that lead

phosphates are thermodynamically predicted to effectively control lead solubility in pure water

especially at slighly acidic to slightly alkaline conditions. The situation is dramatically improved

when realistic levels of chloride and phosphate are assumed to be present in ground or surface
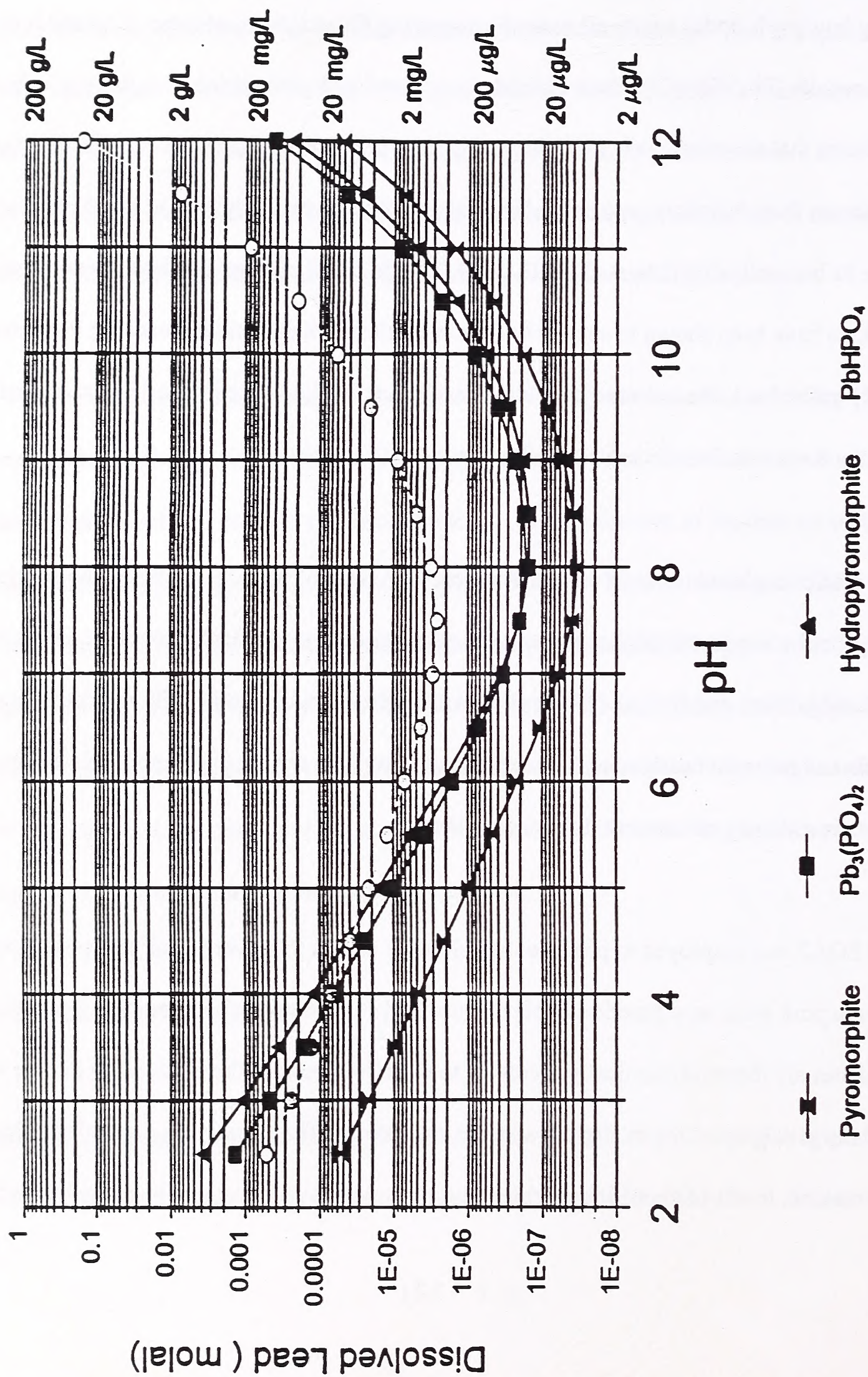
Figure 3-5. Solubility of lead phosphates in distilled water as a function of pH as predicted by MINTEQA2. Each curve represents the amount of lead that dissolves from a particular lead phosphate mineral phase as a function of pH.

water. The use of phosphates will be further discussed as a potential option for controlling lead mobility at shooting ranges (Chapter 5).

3.2.2.5 Summary of Precipitation/Dissolution Processes

Generally, lead carbonate, lead hydroxyl carbonate, or lead hydroxide will be the precipitates encountered on shooting ranges. These solids are primarily controlled by pH and the concentrations of carbonate and sulfate. Dissolved lead concentrations are effectively controlled at neutral to slightly alkaline pH (7 to 9). Acidic pHs (< 7) on the other hand, can give rise to relatively high dissolved lead concentrations. Other precipitates may affect the solubility of lead. In particular, lead sulfides can control both solubility and bioavailability of lead in reducing sediments and soils. Lead phosphates are also highly insoluble and effectively control dissolved and bioavailable lead in oxygenated sediments over the range of pHs in the environment. While site-specific conditions will determine the precipitates present at any particular site, lead carbonate and lead sulfate will generally dominate. These precipitation processes may not eliminate concerns about the mobility of lead, but adsorption processes (Section 3.2.3) will further reduce dissolved lead concentrations.

3.2.3 Adsorption/Desorption Processes

3.2.3.1 Definition

Adsorption is the process through which dissolved ions are taken out of solution by binding to the surfaces of soil/sediment particles in contact with the solution. Adsorption decreases the amount of dissolved materials present in solution. Desorption is the opposite of adsorption and refers to the release of bound species from a particulate surface back into solution. The distribution coefficient, K_d is the ratio of material adsorbed to the amount remaining in solution. The higher the value of K_d, the higher the proportion of material adsorbed and the lower the proportion dissolved in solution. Cation exchange capacity (CEC) is another measure of a soil or sediment's capacity to adsorb positive ions (cations) from solution. This type of adsorption involves the exchange of weakly adsorbed cations for more strongly adsorbed cations. Dissolved lead generally exists in a cationic form Pb^{+2} and will adsorb to cation exchange sites.

3.2.3.2 Environmental Significance of Adsorption/Desorption Processes

Adsorption is an important process in the environment that effectively limits the dissolved concentration of chemicals in many circumstances. Typical soils and sediments contain a large number of effective sorbents such as iron-manganese (Fe-Mn) oxides, organic matter, and clays.

For some chemicals, this is the most important determinant of dissolved concentrations.

Additionally, adsorbed chemicals are generally considered to be less bioavailable, and therefore

less toxic.

3.2.3.3 Factors Affecting Adsorption/Desorption Processes

Adsorption/desorption processes are controlled by several complex and interactive parameters.

The parameters that affect the adsorption of lead include pH, concentration of lead, and

concentration of competing ions, amounts and types of sorbent phases, and the amount of lead or

competing ions already adsorbed. In general, conditions leading to a large K_d (more binding) are

neutral to slightly alkaline pHs, high sorbent levels, and/or low concentration of competing

species.

3.2.3.4 Chemistry of Adsorption/Desorption Processes

Adsorption is the process by which lead ions bind to surfaces of solids in water, soils, and

sediments. This process is another means by which common soil and sediment constituents can

ultimately control the dissolved concentration of lead. Adsorption processes are also of

importance because strongly adsorbed lead has been shown to be relatively unavailable to biota

(Gunn 1989). Lead has been shown to bind to a variety of soil constituents including iron and

manganese oxyhydroxides, carbonates, clay particles, organic matter, and sulfides (Rai et al.

1984). Adsorption of lead is generally dominated by Fe-Mn oxyhydroxides, carbonates, organic

matter, and/or clay. Unfortunately, both the adsorptive capacity and distribution coefficient K_d

vary widely. The adsorption of lead can be affected by solution chemistry in that pH, ionic

strength, and complexation all influence the distribution coefficient (Rai et al. 1984).

Adsorption processes in the environment are complex and the interplay of different adsorption

processes within soils and sediments is not necessarily well understood. There are several

common approaches to conducting research in this area.

- The first of these approaches is to collect soil/sediment samples and to allow them to

  equilibrate with solutions in batch or column experiments. These experiments can rely

  on adsorption (solutions spiked with lead) or desorption processes (solutions

  representative of pore water without lead), or soils/sediments and associated pore waters

  can be collected and studied directly. These data can then be fit to simplistic adsorption

  models such as Freundlich or Langmuir isotherms.

- The second approach is to identify discrete adsorbents and study each separately, creating

  thermodynamic relationships that lend themselves to extrapolation to naturally occurring

  soils and sediments.

- A third approach is to collect information on adsorbent levels in field samples, as well as other chemical data, and then perform a statistical analysis of the data with the goal of identifying and quantifying the importance of each of the phases.

- A fourth approach is to employ an analytical technique called "sequential extraction" to gain insight into the quantity of lead that is bound with each phase.

There are benefits and difficulties associated with each of these approaches. Several additional complicating factors exist including the presence of lead precipitates, the presence of solid-solution phenomena, irreversible sorption processes, lack of equilibrium due to the kinetics of the processes, preservation of soil/sediment chemical conditions, etc. All of these factors can complicate the results. As a result, caution should be exercised in using data from the discussions that follow.

Numerous studies have shown that lead strongly sorbs to sediment/soils in a variety of settings. The low mobility of lead in sediments is well demonstrated by sediment dating through measurement of the isotope ^{210}Pb. Wieland et al. (1993) estimated that the K_d for ^{210}Pb in the water column in Lake Sempach was 1.1×10^6 L/kg (indicates very strong adsorption and low mobility). Talbot (1989) showed that lead was strongly associated with suspended sediments in Port Phillip Bay, Australia.

Stansley et al. (1992) studied the mobility and levels of lead in surface water at trap and skeet ranges and reported that they saw little or no mobility of lead via surface water at neutral to alkaline pH. Significant filterable lead was found in one shot fall zone on one range. These results suggested that lead could potentially be desorbed at lower pH.

Low pH environments are highly variable in their effect on lead mobility. Griffin and Shimp (1976) reported that different landfill leachates caused significant changes in the effectiveness of clays in adsorbing metals. Although a number of factors are responsible for the observed effect, pH was thought to be the dominant factor. Dredged sediments that were allowed to dry and oxidize were shown by Saeki et al. (1993) to readily release cadmium, but lead was mobilized to a much lesser extent. Presumably this is due to lead released (as the sulfides are oxidized) being readily adsorbed by the sediments even at lowered pH. Nelson and Campbell (1991) prepared a critical review with specific attention to the effects of acidification on the geochemistry of Al, Cd, Hg, and Pb in freshwater environments. They showed that acidification resulted in the release of a variety of materials in an effort to buffer the pH.

Turner et al. (1985) studied the biogeochemistry of lead in the New Jersey Pine Barrens and found that the bulk of atmospherically deposited lead was strongly adsorbed by soils and little or no lead percolated beyond 2-m soil depth. The limited mobility of lead in water was strongly correlated with dissolved organic carbon levels. Further, little accumulation of lead by plants

was detected. In another study, Wang et al. (1995) employed "clean" analytical techniques to investigate lead levels in northern hardwood forested ecosystems. They concluded that earlier measurements that did not use clean techniques overstated lead concentrations in streams by 10-100 times. Dissolved lead levels were found to be <10 parts per trillion and the authors concluded that lead did not move out of the forest soils. Similarly, Dumontet et al. (1990) reported that lead did not appear to be significantly mobile in low pH acidic virgin peat soils located near a smelter. The majority of the lead was found in the upper 0-15 cm layer and at significantly lower concentrations at depth. This is nearly a worst case scenario in that lead is expected to be most mobile at low pH. In contrast, Martin and Coughtrey (1987) investigated the cycling of lead in a woodland ecosystem in New Jersey and concluded that metals (including lead) are lost from the soil as pH decreases.

Several authors have proposed simple models for the purpose of predicting the adsorption of lead. Hem (1976b) presents a model for the prediction of sediment and water lead levels as a function of cation exchange capacity (CEC) and pH. There are several limitations to this model but it predicted Pb^{2+} concentrations within a factor of 10 of measured values for the cases tested. This model predicts that dissolved lead would be less effectively adsorbed by sediments at low and high pH. Harter (1979) reported that a summation of bases is a better predictor for several northeastern soils than CEC because it includes contributions from both pH and CEC. Zimdahl and Skogerboe (1977) present a comparison of soil CEC and adsorption and report that lead

adsorption can be related to both CEC and pH. Note that this study evaluated 17 soils from Colorado which were spiked with lead and allowed to equilibrate for 48 hours. On the other hand, Korte et al. (1976) suggest that pH, iron oxides, texture, and surface area provide a better estimate of adsorption than CEC. Gerritse and Van Driel (1984) provide a similar relationship based on organic matter and pH based on behavior observed with 33 temperate soils from the Netherlands, Britain, and France.

3.2.3.4.1 Sorption/Desorption Experiments

Studies that involve the spiking of sediments with metal solutions to measure the sorptive capacity of the sediments tend to overestimate dissolved concentrations. The problem arises from a lack of equilibrium at the end of the study period (Tuin and Tels 1990). Much of the lead initially adsorbed is associated with CEC and is often released in a subsequent desorption study. After some time, however, the lead is presumably readsorbed to stronger adsorption sites or diffuses into the particles. Conversely, studies that involve desorption of lead already present may overestimate adsorption for similar reasons.

The kinetics of adsorption processes can affect the ultimate mobility of lead. Bunzl (1974a, 1974b), and Bunzl et al. (1976) have investigated the kinetics of ion exchange by humic acid and

peat with a variety of metals and determined that the rates of adsorption were fastest for lead and slower for less strongly bound ions.

Elkhatib et al. (1991) investigated the sorption capacity of three different Egyptian soil types for lead and fit the data to Langmuir and Freundlich isotherms. The soils ranged from a calcium carbonate rich soil (Langmuir b = 773 mmol Pb/kg) to a sandy soil (Langmuir b = 435 mmol Pb/kg); precipitation and adsorptive effects were not distinguished. The study attempted to examine the effect of temperature on adsorption and concluded that adsorption increased with temperature. Since temperature also tends to increase reaction rates and diffusion rates, it is not clear whether the temperature dependence observed is indicative of a change in adsorption with temperature.

Abd-Elfattah and Wada (1981) spiked calcium saturated soil samples with a variety of metals and measured the remaining dissolved concentrations after equilibrium was established. They reported that the soil preferentially adsorbed lead and that the selectivity coefficient calculated using calcium as a reference ion increased with mineral phase in the order montmorillonite < humus, kaolinite < allophane, imogolite < halloysite, iron oxides. This study demonstrates that lead competes with calcium to differing degrees depending on the mineral phases present in the soils.

3.2.3.4.2 Pure Sorbent Phase Studies

The study of pure phase adsorption relationships lends itself to a clearer understanding of how lead will interact with each of the discrete phases. This approach allows extrapolation to more complicated systems containing multiple sorbents and competing ions and is much more useful in developing thermodynamic models. The limitation is that natural soils are not used and determinations of total organic carbon, amorphous iron oxyhydroxide, etc. do not readily lend themselves to addressing how much of one material might actually be coating another type. Further complications arise when studies rely on synthetic materials which may not be representative of natural surfaces.

Rai et al. (1984) summarize a substantial number of lead adsorption parameters for different phases and mixtures. The data are presented according to the modeling approach employed by the original author and are not necessarily directly comparable. The authors report that the apparent binding energies do not vary substantially between phases but that adsorption capacity of individual soils is based on the constituents in soil. Mn oxides generally have the capacity to adsorb the highest quantity of lead followed by Fe oxides > organic matter > clay minerals.

Hatton and Pickering (1980) studied the impact of pH on the binding of Cu, Pb, Zn, and Cd by clay-humic acid mixtures. In this study, relatively pure phases of the clays illite, kaolinite,

montmorillonite, and two types of humic acid were combined in varying quantities. At pH < 6, the adsorption of lead was correlated to the sum of the individual substrate adsorption values. At pH > 6, the lead hydroxyl anion dominated the adsorption process (doubling the amount of lead that could be adsorbed) and effectively competed with the complexation effect of humic material solubilized at the elevated pH. Scrudata and Estes (1975) showed that clays are less effective adsorbers of lead at acidic pH than under neutral conditions. Griffin and Au (1977) showed that calcium effectively competes with lead for adsorption sites on clays. Bittle and Miller (1974) studied the degree to which calcium competes with lead and reported selectivity coefficients for Pb-Ca exchange on montmorillonite, illite, and kaolinite as 0.60, 0.44, and 0.34, respectively.

A number of authors have studied the adsorption of lead by manganese and/or iron oxyhydroxide surfaces. Dzombak (1986) presents a detailed analysis of experimental sorption data for a number of cations and anions. These data were used to generate parameters for use in a diffuse-layer approach to modeling sorption. A portion of these fitting parameters including lead are input into U.S. EPA's MINTEQA2 model (U.S. EPA 1990). These constants indicate that lead is strongly adsorbed by amorphous iron oxyhydroxide phase and that the behavior is strongly pH dependent. In general, cationic metals such as lead were more strongly adsorbed in neutral to alkaline conditions.

Gadde and Laitenen (1974) studied the adsorption of lead to metal oxyhydroxide phases. In this study, it was shown that manganese oxides would continue to bind lead at low pH compared to iron and aluminum oxyhydroxides which typically release lead under these acidic conditions. The binding strength for lead was $Mn > Fe > Al$. McKenzie (1980) also presented binding studies of manganese and iron oxides and indicated that strong specific adsorption and/or precipitation of Pb-Mn compounds (although precipitation was not observed) may account for the observed behavior. McKenzie (1980) observed a stronger specific adsorption of lead to the mineral hematite than to the mineral goethite. Swallow et al. (1980) investigated the possibility that aging, ionic strength, or the use of different electrolytes might alter the adsorption behavior of synthetic amorphous iron oxyhydroxides and found that these factors had little effect. This suggests that lead sorption to amorphous iron oxyhydroxide may be estimated in a consistent manner for a variety of conditions. Forbes et al. (1976) investigated the adsorption of lead by goethite and presented a model and suggested parameters that provide a means of modeling sorption by goethite.

3.2.3.4.3 Sequential Extraction Studies

Sequential extraction is an analytical approach where soil or sediment is sequentially exposed to a variety of solvents. Each solvent removes a portion of the material present in the soil or sediment and the resulting solution is collected for analysis. The collection of sequential

extraction data has the advantage that it directly examines what portion of the lead is bound to oxyhydroxides, clays, organic carbon, carbonates, etc. The disadvantage is that the boundaries between exchangeable, carbonate, iron/manganese oxyhydroxides, organic carbon, and inert phases are not quite so clearly established as some studies might suggest. Ions compete for adsorption sites on carbonates, organic carbon, and amorphous oxyhydroxides and the addition of magnesium ions to release the "exchangeable" fraction will release a portion of the material bound to other phases. As an example, when the pH is lowered to dissolve material that is "bound" to carbonate, a significant portion of the material adsorbed to iron oxyhydroxide may be released simultaneously.

Yong et al. (1993) presented a summary of seventeen different sequential extraction procedures and readily acknowledge the limitations of these procedures in successfully releasing only the targeted phases. Yong et al. (1993) also maintain the value of these studies in providing estimates of metal adsorption by natural and synthetic soils and their potential to subsequently release the materials under adverse conditions.

Of the extraction procedures, the method of Tessier et al. (1979) tends to be the most widely applied. Lopez-Sanchez et al. (1993) reported the comparison of their own sequential extraction procedure and compared its results with those employing Tessier et al. (1979). The Lopez-

Sanchez et al. (1993) report details significant differences in findings as a result of relatively subtle experimental differences.

The examination of soils employing these sequential extraction methodologies shows that Fe-Mn oxyhydroxides, carbonates, and organic/sulfidic phases dominate the sorption of lead. Because there are numerous types of phases in these experiments, and conditions controlling which of the individual phases will dominate vary substantially, there is contention over which phase is the best estimate of adsorption. The lead associated with these phases may also be present as a precipitate that is soluble in the course of the extraction experiment. The lead can also be found in the residual phase which is generally considered relatively inert and probably not of environmental significance.

Yong et al. (1993) sequentially extracted relatively pure clay fractions treated with lead and observed that portions of lead are recovered from each of the different extracts. This demonstrates that sequential extraction methods are not entirely successful at targetting the responsible phase. Yong et al. (1993) and Yong and Phadungchewit (1993) provided measurements of the amount of lead adsorbed by these clays over a range of pHs and show that acidic pHs favor enhanced lead mobility.

Ramos et al. (1994) investigated several metals in soils from Donana National Park, Spain by sequential extraction methods and found that lead was primarily associated with iron oxides and not the organic phase. Howard and Sova (1993) examined several soils near a highway in Michigan and reported that organic, carbonate, and Fe-Mn oxide phases are the dominant sorbents of lead in this environment. The study also looked at phase concentration factors (PCFs) and reported that lead PCFs are ordered Fe-Mn oxide > carbonate > organic. This ordering corresponds to the relative affinity of these phases for lead. Fe-Mn oxides have a very strong specific adsorption affinity for lead.

Tuin and Tels (1990) examined the distribution of six heavy metals in clays before and after extractive cleaning using the sequential extraction procedure of Tessier et al. (1979). This study showed that most lead added to the soils adsorbed onto the exchangeable, carbonate, and/or Fe/Mn oxide fractions. Metals present in the soil for some time can be much more strongly adsorbed, and may not be efficiently extractable by 0.1 N HCl or EDTA washing in the order carbonate < metal oxyhydroxides < organic/sulfide < residual.

Sediment studies tend to follow the soil results fairly closely. The reports detailed below show that non-residual lead is commonly associated with organic/sulfidic phases and Fe-Mn oxyhydroxide phases. At lower lead levels, the role of Fe-Mn oxyhydroxides tend to be greater

while at elevated lead levels organic/sulfidic phases may dominate. This is probably due to the presence of lead sulfide precipitates in the sediments.

Elsokkary and Muller (1990) studied contaminated sediments from the River Nile, Egypt and reported that lead was bound in the organic/sulfide, reducible oxide, and residual phases. The authors noted that in samples with lower lead levels the reducible phase played a more important role, while at higher levels of lead the organic/sulfide phase dominated. This would tend to support the conclusion that sulfide precipitates form at the higher levels and/or that the reducible phase may bind lead stronger than the organic phase. The implication of this would be that low lead scenarios would be dominated by Fe-Mn oxide adsorption processes and that organic matter may drive in moderate to high lead scenarios.

Ton et al. (1993) demonstrated that lead in Florida wetlands are associated with organic carbon and some will be present as sulfide precipitates. A relatively small portion was in a readily exchangeable form. Abu-Hilal (1993) employed the methods of Tessier et al. (1979) to study the partitioning of metals in surficial sediments in the Gulf of Aqaba, Jordan, and reported that the bulk of lead (36 to 82%) is associated with the Fe-Mn oxide phase and that the organic phase can also play a role (19-35%). Schintu et al. (1991) investigated stream and lake sediments in Sardinia and reported that 58% of lead in river sediments is bound in Fe-Mn oxides and 32% in carbonates. In lake sediments this changes slightly with 45% in Fe-Mn oxides, 21% in

exchangeable + carbonate, and 29% in organic phases. Pardo et al. (1993) examined sediments in two rivers in Spain and reported that most of the lead is associated with the Fe-Mn oxide phase (45 and 51 %), carbonates (17 and 17%), and organic matter/sulfides (22 and 18%). In another study in Spain, Ruiz et al. (1991) reported nearly 70% of lead is bound to Fe-Mn oxides.

3.2.3.4.4 Statistical Treatments

The statistical analysis of large data sets is useful for establishing a site specific relationship for extrapolation between conditions. One limitation, however, is that vast quantities of data are needed to form a good foundation for an analysis of variance (ANOVA) analysis. Another limitation is that adsorption and precipitation reactions are by nature, highly non-linear and may not be well characterized by traditional statistical analyses. A further limitation is that statistics can be used to establish a relationship between observations but do not directly assign cause-and-effect relationships. It is interesting to note that many sequential extraction studies seem to indicate that Fe-Mn oxides are of greater importance than organic matter while statistical studies seem to indicate that the opposite is true.

Soldatini, et al. (1976) examined lead adsorption on 12 different soils from Tuscany, Italy. The data were found to fit Langmuir and Freundlich isotherms over a broad range of concentrations. Statistical analysis of the isotherms indicated correlations between Langmuir "a" values and soil

parameters and show the correlation is strongest in the order CEC > manganese > iron > organic matter. The authors state that an "all possible regressions" analysis revealed that only CEC and organic carbon are responsible for the adsorption behavior. In a related paper, Riffaldi et al. (1976) showed that calcium can effectively compete with lead for binding sites, making lead more mobile.

In contrast, King (1988) statistically examined the retention of metals by several soils from the southeastern United States and found that lead was generally strongly sorbed. He concluded that Al and Mn oxides are related to the sorption of metals in these soils but not nearly so strongly as Fe oxide. King (1988) suggests that it would be more appropriate to model the sorption of lead in these soils based on Fe oxides and pH instead of CEC.

3.2.3.5 Summary of Adsorption/Desorption Processes

Studies designed to investigate the sorption of lead tend to indicate that organic carbon, Fe-Mn oxides, clays, and carbonates are the dominant sorbent phases. The relative importance of these factors is highly dependent on the type of study conducted and site-specific parameters. The dominant solution parameters affecting adsorption are pH, dissolved lead concentration, and concentration of competing ions (e.g. Ca^{+2}, Mg^{+2}). These parameters are site-dependent and as a result, K_d for lead has been shown to vary over several orders of magnitude (<1.0 to 10,000,000

L/kg). Generally, lead is found to strongly adsorb to sediments and is not mobile under most conditions. Acidic pH, high lead concentrations, presence of competing ions, and low sorbent levels give rise to the situation where mobility is the greatest.

3.2.4 Complexation/Chelation

3.2.4.1 Definition

Complexation and chelation are chemical processes by which metal ions combine with other dissolved constituents to form a new dissolved species. In contrast, adsorption refers to the association with solid particles. These processes tends to allow more of the metal to dissolve in solution.

3.2.4.2 Environmental Significance of Complexation/Chelation Processes

Complexation can substantially increase dissolved concentration of metals in solution and care must be taken to identify potential complexing agents.

3.2.4.3 Factors Affecting the Complexation/Chelation Processes

The presence of potential complexing agents is the only factor that significantly affects whether complexation will occur. Potential complexing agents include EDTA, NTA, and fulvic acid. Of these, fulvic acid is the only one that is likely to be encountered on a shooting range since it is a naturally occuring material. While EDTA and NTA are strong chelating agents, they are not likely to occur on shooting ranges in a quantity necessary to significantly affect mobility.

3.2.4.4 Chemistry of the Complexation/Chelation Processes

Dissolved lead is commonly present as Pb^{2+} and a variety of complexes including chlorides, carbonates, and hydroxides. The formation of these species can be predicted readily from thermodynamic data (Rai et al. 1984; Hem 1976). These inorganic complexes of lead generally do not substantially affect the solubility of lead except as previously described. This section will focus on other types of sorbents that can substantially alter the solubility of lead.

A number of additional species may form complexes with lead or may chelate lead and enhance the quantity that dissolves in water including organic acids, fulvic material, EDTA, NTA, etc. (Peters and Shem 1992). Many of these species are unusual in occurrence and are not present in substantial quantities in most areas. Others, such as fulvic acids may be present much more often

in soils and sediments. Saar and Weber (1980) presented formation constants for lead-fulvic acid complexes and point out that lead-fulvic acid complexes may precipitate, thus limiting the impact of fulvic acids on lead solubility.

Alloway et al. (1984) studied the speciation of lead and cadmium in the <0.45 micron soil solution fraction. The authors passed samples of pore water through a series of columns specially designed to measure what quantity of dissolved lead was present in anionic, cationic, neutral, and/or organic forms. The majority of lead was present as cationic species with one case where neutral lead (aqueous $PbCO_3$ is a possibility) was found. A small fraction, <10% of the lead was associated with organic complexes.

Denduluri (1993, 1994) investigated the bioavailability of lead chelated with EDTA and NTA to plants. Although EDTA and NTA will chelate with lead and allow it to become mobile, it is apparent from these studies that the availability of chelated lead is significantly reduced over non-chelated forms. On the other hand, Athalye et al. (1995) did not observe significant differences between the uptake of chelated and non-chelated lead by plants.

Turner et al. (1985) studied the biogeochemistry of lead in the New Jersey Pine Barrens and found that the bulk of atmospherically deposited lead was adsorbed by soils and little or no lead percolated beyond 2 m of soil depth. The mobility of lead in water was strongly correlated with

dissolved organic carbon levels (potentially as fulvic acid complexes). Further, little

accumulation of lead by plants was detected.

3.2.4.5 Summary of Complexation/Chelation Processes

Complexation can occur on shooting ranges if complexing agents such as EDTA, NTA, and/or

fulvic acid are present. Out of this group, only fulvic acids are a naturally occuring material.

While these materials can complex lead and make it more soluble they may actually reduce

bioavailability. Every species of lead has its own toxicity due to the fact that absorption rates

and the mode/expression of toxicity are different. High molecular weight chelated forms of lead

may not be readily absorbed by biota and are therefore less likely to produce a toxic effect.

3.3 SELECTED APPROACHES FOR ESTIMATING LEAD MOBILITY

K_d values have been calculated using models in a nation-wide context for soil types in the United

States. Results indicate that the distribution coefficient for lead can vary over several orders of

magnitude (<1.0 L/kg to 10,000,000 L/kg, unpublished results, Novo-Gradac) depending on the

amorphous iron oxyhydroxide, organic carbon, pH, and lead levels. These results indicate that

adsorption is an important process in determining lead fate and transport and is dependent on

site-specific conditions. As a result, only generalizations regarding lead mobility may be made without site-specific information.

Each of the four basic processes described in Section 3.2 play a role in determining the mobility of lead in the environment. Ruggaber et al. (1990) used MINTEQA2 and MULTIMED (a transport model) to describe the mobility of lead from a lead battery CERCLA site. In this case study, MINTEQA2 was first used to predict which primary solubility controls would be present at the source of contamination using site-specific chemistry data. A variety of minerals were predicted including anglesite, cerussite, and larnakite ($PBSO_4 \cdot PbO$). These solids determined the maximum concentration of dissolved lead at the source. MINTEQA2 was also used to estimate the K_d value for dissolved lead in the aquifer based on the diffuse-layer model and adsorption to amorphous iron oxyhydroxide (Dzombak 1986). These calculations were performed for both the unsaturated and saturated zones at different pH levels and at different target cleanup levels. The no action alternative yielded low K_d values for lead (0.5 and 104 L/kg) in the unsaturated and saturated zones, respectively. These K_d values are indicative of relatively low adsorption. In comparison, moderate values (176 and 1000 L/kg) were used in the unsaturated and saturated zones, respectively when a 1,000 mg/L action level was chosen. This reference provides a relevant example of how to effectively use speciation approaches to address fate and transport concerns.

Other authors have used speciation modeling approaches as an effective method of estimating the bioavailable fraction of lead in soil/sediments. Ruby et al. (1992) and Davis et al. (1992) reported that in vitro tests using lead acetate tend to overestimate the uptake of lead by at least a factor of five. In contrast, they found that MINTEQA2 estimates of the available portion provided better agreement with field data. Kinetic limitations also influence the adsorption rate and these are not directly addressed by MINTEQA2.

Yanful et al. (1988a, 1988b, 1990) present a series of papers where several geochemical concepts were employed to investigate the mobility of lead through a clay liner at a landfill. Yanful et al. (1988a) presented a thermodynamic assessment designed to investigate potential solubility controls. Lead carbonate was thought to be present and to control solubility in the pH 7.8 to 8.0 range. Lead was shown to not be significantly mobile and moved only 10 to 20 cm into the clay barrier whereas chloride moved 130 cm. Yanful et al. (1988b) employed sequential extraction approaches to study the association of lead with a variety of phases and found most of the lead was associated with carbonates. This was consistent with the Yanful et al.'s earlier findings. They also compared binding in carbonate free soils to those present at the site and reported that binding should be greater in carbonate containing soils. Yanful et al. (1990) rebuts comments suggesting that dissolved organic carbon (DOC) significantly enhanced lead mobility and as proof noted that DOC had moved significantly further through the clay barrier than lead.

3.4 FIELD STUDIES EXAMINING THE MOBILITY OF LEAD AT SHOOTING RANGES

Only a few published studies have attempted to measure or identify the extent of lead mobility at shooting ranges. Studies published to date have indicated a general lack of lead mobility under a variety of environmental conditions. For example, a study performed at the Lincoln Park Gun Club on Lake Michigan indicated that although sediments high levels od lead from 73 years of trap and skeet shooting, lead concentrations in water overlying these sediments were below the Lake Michigan lead water quality standard of 50 μg/L (Pott et al. 1993). Pott et al. (1993) also observed no significant correlations between lead shot and TCLP lead, supernatant lead, and total lead fractions. The lack of correlations were hypothesized to be the result of the relative inertness of the metallic lead pellets combined with other anthropogenic sources of lead. In addition, Pott et al. (1993) observed little evidence of movement of lead to offsite areas in Lake Michigan. Although sediment and water characteristics were not provided, these results suggested that under the likely reducing conditions in near shore Lake Michigan sediments, lead was relatively immobile.

Stansley et al. (1992) examined the mobility of lead at six trap and skeet ranges in open water and wetland areas in New Jersey. Of the ranges examined, no correlation was found between total lead concentrations in water with pH, alkalinity, or shot density. Further sampling at two

ranges indicated that approximately 94% of lead in surface water was removed by filtration (i.e.,

only 6% was in the dissolved fraction). These data indicated that most of the lead in surface

water was attached to suspended particulates in the water column and settled out within a short

distance from the shotfall zone. Further evidence indicated that downstream lead concentrations

were similar to reference areas not influenced by the shooting range. In one shooting range

located in a marsh where the pH of the water was 6.3 (alkalinity = 20.5 mg/L as $CaCO_3$), lead

concentrations were substantially elevated (total lead = 1,270 ug/L; dissolved lead = 83 ug/L). In

other wetland and open water areas where the pH ranged from 7.0 to 8.4 (alkalinity ranged from

7.9 to 20.2 mg/L as $CaCO_3$), total and dissolved lead concentrations in surface water were below

detection limits (1.0 μg/L). There was no evidence of bioaccumulation of lead in sunfish and

largemouth bass in these waters and all tissue concentrations were below the limit of 0.3 μg/g

(fresh weight) recommended by the World Health Organization (WHO) for human consumption

(Stansley et al. 1992). These data indicated that no offsite transport of lead via surface water at

neutral to alkaline pH (7.0 to 8.4) at shooting ranges was observed. In a slightly acidic marsh

where the pH of water was 6.3, lead showed a propensity to mobilize into surface water within

one shotfall zone.

The fate of lead was examined in a western Australian wetland (pH range 8.0-9.4) used for duck

hunting and characterized by alkaline, hard water (alkalinity and hardness data not given) (Lund

et al. 1991). A nature reserve (pH range 6.1-8.6) without shooting was also studied for

comparison. Sediment concentrations from the hunting wetland were not significantly different from sediments in the nature reserve and were low enough to be considered as background levels. Bioaccumulation data from macroinvertebrates and rooted aquatic vegetation indicated no evidence of lead biomagnification in the wetland used for duck hunting. The results indicated that metallic lead was not transformed and did not cycle within a wetland ecosystem with pH ranging from 8.0 to 9.4.

In a terrestrial system characterized by a 4 cm thick surface humus layer, the fate of lead from lead shot to soil humus and plants was examined (Manninen and Tanskanen 1993). After screening out shot, humus (pH range = 5.6-5.9; percent organic matter = 41-61%) contained up to 38,000 mg/kg of dissolved (EDTA extractable) and total lead. Although considerable quantities of lead accumulated in the soil humus layer, terrestrial plant uptake to leaves was minimal. The poor translocation of lead from roots to shoots in many species of plants likely explained such low lead content in leaves (Manninen and Tanskanen 1993). The results indicated that lead was mobilized into acidic soil humus as might be expected, but that this did not result in food chain uptake by plants.

From the relatively few studies conducted on lead mobility in shooting ranges, pH appears to be a contributing factor. Attempts to correlate lead concentrations in water with pH, alkalinity, or shot density were not successful, likely due to the influence of other environmental factors (e.g.,

flow rate, sediment pH, sorption). Surface water pH values of ≥ 7.0 tend to indicate restricted lead mobility whereas pH values of ≤ 6.5 indicate enhanced lead mobility. Besides pH, demonstrated effects of other environmental variables in field studies on lead mobility at shooting ranges remains unknown.

3.5 SUMMARY

Bullets and shot are composed primarily of metallic lead which is slowly released to adjacent soil through a variety of "weathering" processes. If metallic lead was inert in the environment, it would not dissolve and would not be expected to be transported by any chemical means. However, metallic lead is slowly oxidized (corroded) to forms that dissolve and becomes slightly mobile in the environment. The rate at which metallic lead will oxidize and migrate to the water column is therefore very slow. Complete corrosion of bullets and shot through oxidation and dissolution may take as much as 100-300 years or longer. Furthermore, the dissolution process can be counteracted by precipitation as lead minerals or adsorption to naturally occuring mineral phases. These processes are extremely site-specific.

Minerals that are important in controlling dissolved lead concentrations via precipitation in oxidizing to slightly reducing environments (typical of most soils, surface waters, and groundwater) include lead hydroxide, carbonates, phosphates, and sulfates. The pH of water is

important in determining which mineral species will dominate and what the dissolved lead concentration will be. Equilibrium modelling with carbonate and sulfate present at millimolar levels predict that dissolved lead concentrations will not exceed 10 ppb at pHs greater than 7.5, but exceed 50 ppb at pHs below 7.0 and 1,000 ppb at pHs below 6.2. If sulfate or carbonate levels are different or additional lead-controlling precipitates are present, the predicted dissolved lead concentrations can be altered significantly. In reducing environments (typical of sediments, flooded soils, and some ground water) insoluble lead sulfide effectively controls dissolved lead concentrations.

Important materials which adsorb lead include organic matter, iron and manganese oxyhydroxides, clays, carbonates, and sulfides. It is well established that the distribution coefficient (K_d) describing this behavior is dependant on the nature and type of adsorbents present, the pH, the concentration of lead, and the concentration of other ions that are competeing for binding sites in these materials. The value of K_d can vary over several orders of magnitude (< 1.0 to over 1,000,000 L/kg) depending on these factors and is often non-linear over the range of interest (Ruggaber et al. 1990; Hem 1976; Rai et al. 1984). This broad range of K_d values can greatly complicate examinations of the mobility of dissolved lead, and the simplistic approaches often employed can greatly exaggerate dissolved levels (Ruggaber et al. 1990).

Lead mobility will be controlled by adsorption under the majority of conditions found on shooting ranges. In general, neutral or slightly alkaline conditions are expected to give rise to low mobility conditions and only acidic conditions or cases where low amounts of adsorbants are present would result in significant mobility.

Two further complicating factors are present that may increase mobility. These are complexation/chelation and transport of small particulates that contain adsorbed lead, the latter being a physical transport mechanism. While this is true, it should be understood that chelation by many compounds (e.g., EDTA, which is not present in nature) has been shown to decrease the bioavailability of lead (Denduluri 1993, 1994). Particulate transport mechanisms may be effective in altering the distribution of lead at a site over time but likewise may not have a substantial effect on bioavailability. It should be emphasized that most chelating agents are not present at shooting ranges and that only naturally occurring materials (such as fulvic acids) are likely to be present.

Geochemical equilibrium software such as EPA's MINTEQA2 model are available to estimate water concentrations of lead given site-specific conditions, but such predictions can be subject to errors due to (1) lack of appropriate site information, (2) kinetic limitations, and (3) oversimplification of the geochemical problem. For example, geochemical modeling approaches

have been shown to overestimate dissolved lead concentrations when only

precipitation/dissolution processes are considered.

CHAPTER 4. OPTIONS FOR CONTROLLING LEAD MOBILITY AT SHOOTING RANGES

There are several options for effectively controlling lead mobility at shooting ranges. At some ranges, conditions will be such that efforts to control mobility will not be warranted. At other locations where control might be considered, site-specific conditions may favor some techniques over others. The approaches presented below are discussed at a conceptual level based on the preceding sections of this document and are limited to options that could be used for managing lead mobility at operating ranges. Cleanup of ranges at the end of their use is not considered. The effectiveness of some control options is well documented, while others seem reasonable but little documentation exists as to their effectiveness. The mobility control techniques considered below include: recovery/recycling, control of storm water runoff, vegetative planting, clay layers, lime addition, phosphate addition, addition of other natural or synthetic materials, soil capping, and cultivating/tilling.

4.1 RECOVERY/RECYCLING

Periodic recovery and subsequent recycling of lead shot and ammunition at shooting ranges provides an important and cost-effective option for reducing lead mobility, as the total mass of lead that can be potentially mobilized is reduced. Basically, the process involves soil excavation and subsequent physical separation of shot and/or bullet fragments, usually by screening. The recovered lead is transported offsite for recycling, and the soil is often replaced to its original contours.

The advantages of recovery and recycling are that it periodically removes much of the mass of lead from the environment at the range, and hence greatly reduces the amount of lead available for potential mobilization. The monetary value of the recycled lead can help offset the costs involved. The disadvantages are that typically there is no attempt to recover lead from all areas (e.g., rugged or wooded terrain and areas in front of the backstop berms and near shotgun shooters are typically not considered cost-effective for recovery), and the recovery of shot or bullet fragments is not perfect in the areas that are screened. These factors in combination indicate that a state-of-the-practice recovery operation may not remove sufficient lead to satisfy all environmental concerns. At active ranges, reintroduction of lead often begins immediately after recovery is completed, and may continue for extended periods before the next recovery operation. This is not to deny the value of a regular recovery/recycling program by reducing the

total quantity of lead in the environment, but to point out that such a program alone may not be sufficient to satisfy lead mobility concerns at some ranges. Other management actions during the periods between recovery operations may be advisable.

4.2   VEGETATIVE CONTROL OF STORM WATER RUNOFF

Vegetative control of storm water runoff can be helpful, either alone or in combination with engineering or structural controls, and is much less expensive than these approaches. Vegetative cover slows runoff velocities, allowing more water to infiltrate where soils can retard the mobility of any lead in the runoff. Vegetative cover also retards erosion and transport of fine particulate lead or lead on soil particles (Karr et al. 1990b). Vegetative cover is a relatively low-cost means of reducing potential lead mobility. However, cover can be hard to maintain and may require continuing management mowing effort. The face of backstop berms, particularly directly behind the targets, can require special attention. Vegetative cover would have to be re-established after lead recovery operations. While some kinds of vegetation such as brush and unmaintained grasses reduce the mobility of lead by controlling runoff, they can also serve as attractive habitat for birds and wildlife, and thus potentially increase wildlife exposure to lead. Attractiveness to birds and wildlife can be minimized by regular maintenance of a cover of carefully selected species of grasses and other plants throughout the area containing lead.

4.3   ENGINEERING CONTROL OF STORM WATER RUNOFF

Engineering or structural control of storm water runoff may be helpful, especially at sites where

lead is widespread, or at sites covered with natural or man made obstructions which restrict

excavation or recovery of lead (Novstrup et al. 1992). Transport of particulate lead and lead on

soil particles can be restricted by settling basins constructed at the site boundary to remove

particles from surface runoff by sedimentation. Advantages are that properly designed settling

basins can be very cost-effective in removing particulate matter, which can transport far more

lead from ranges than can be transported in solution. As the basins fill, sediment must be

periodically removed to maintain efficient performance. The sediment may contain sufficient

lead to be legally classified as hazardous under the Resource Conservation and Recovery Act

(RCRA) if lead exceeds 5 mg/L in the Toxicity Characteristic Leaching Procedure (TCLP) test.

If so, the law requires handling and disposal by trained personnel. For this reason, settling basins

should be used in conjunction with vegetative coverings (Section 4.2) to minimize erosion and

thus reduce the amount of sediment trapped in the basins. Basins should be maintained as long

as lead in runoff is a concern, even if shooting were to cease at the range. If runoff water exiting

the settling basins contained dissolved lead at unacceptable concentrations (i.e., in excess of

water quality standards) management as discussed in the remainder of this chapter may be

necessary (Novstrup et al. 1992).

4.4   LEAD-ACCUMULATING VEGETATION

Some species of plants are more tolerant of lead in soil than others, and some accumulate lead from the soil into their tissues. Some terrestrial plants have been studied for their potential lead "phytoextraction" (Kumar et al. 1995; Bricka et al. 1993). Phytoextraction is a process by which selected plant species are used to reduce soil concentrations of metals such as lead to environmentally acceptable levels (Kumar et al. 1995). Terrestrial plants such as Indian mustard (*Brassica juncea*) have been shown to accumulate up to 55 times the concentration of lead in soil in laboratory experiments (Kumar et al. 1995). In one study, Indian mustard accumulated up to 3.5% lead on a dry weight basis in sprouts. On the reasonable assumption that Indian mustard could produce 18 metric tons/hectare (7.3 tons/acre) of biomass, it could theoretically extract 630 kg of lead/hectare (562 pounds/acre) with a single harvest of above-ground biomass. This concept is particularly attractive since the lead that is available for uptake by such field-grown plants is in forms that would otherwise be of greatest concern regarding potential mobility (Kumar et al. 1995).

The use of metal-accumulating plants for reducing lead mobility in soils at shooting ranges has not yet been adequately demonstrated in practice, and many details remain to be worked out, although there is sufficient basis to warrant further consideration. Potential advantages include relatively low costs, generation of a recyclable lead-rich plant residue, minimal environmental

disturbance, elimination of secondary air or water-borne wastes, and public acceptance (Kumar et al. 1995). These lead-accumulating plants could simultaneously function to control erosion as discussed above. Some potential disadvantages of this approach, aside from the lack of field studies verifying its effectiveness, are that metal-accumulating plants are typically small, slow growing, weedy, and produce low biomass. However, crop plants such as Indian mustard and lawn grasses such as colonial bent grass (*Agrostis tenuis*), centipede grass (*Eremochloa ophiuroides*), and Bermudagrass (*Cynodon dactylon*) have shown considerable lead-accumulation ability in shoots in laboratory studies (Dushenkov et al. 1995; Bricka et al. 1993). These might prove useful in controlling lead mobility at shooting ranges. Management practices such as periodic mowing of vegetation could prevent seed maturity and subsequent ingestion of plants by wildlife species. If the plants were efficient in accumulating lead, the cuttings may, however, contain sufficient lead to be an issue under the Resource Conservation and Recovery Act (RCRA). If cuttings were to be classified as a "hazardous waste", the law requires handling and disposal under rigidly prescribed conditions.

4.5   CLAY LAYERS

Clay minerals have the capacity to adsorb large quantities of dissolved lead in water, soils, and sediments and can act as barriers to lead transport (Hem 1976a; Griffin and Shimp 1976; Yanful et al. 1988). Natural or constructed layers of appropriate types of clay under ranges could be useful in both limiting the infiltration of surface water and effectively immobilizing any lead it might contain. Shallow subsurface clay layers can divert rainwater from infiltration to surface runoff. Dissolved lead in surface runoff can be addressed by other control options discussed in this section. The type of clay is important: minerals with high (80-150 meq/100 g) cation exchange capacities (CEC) such as montmorillonite (smectite) clay can remove up to five times more lead from solution than clays such as kaolinite with low (3-15 meq/100 g) CECs (Griffin and Shimp 1976). Lead removal from solution is primarily cation exchange and adsorption reactions that are affected by pH and ionic competition. At pH values above 6, a substantial increase in lead removal from solution by clay can be expected, due to either increased adsorption of lead-hydroxyl complexes, or formation of $PbCO_3$.

The thickness of the clay liner needed to remove lead from solution depends on the type of clay, solution pH, and lead concentration in solution (Griffin and Shimp 1976). Montmorillonite clay required a much thinner layer to remove lead from solution compared to kaolinite. At pH 5 to 8, a montmorillonite clay liner of 2.0 cm thickness would be enough to remove lead in solution at

concentrations ranging from 10 to 1,000 mg Pb/L. At pH 3, a 10 to 20 cm liner of the same clay would be required for equal removal of lead. Hence, knowledge of the soil pH and the concentration of lead in solution would be required to estimate clay liner thickness effective in removing mobile forms of lead at shooting ranges.

The soil at the range may be a suitable clay, or a clay layer could be brought in during range construction. It may be appropriate to add a surface layer of soil more conducive to plant growth than clay. Adding a subsurface clay layer to an existing range would require considerably more effort then constructing such a layer as part of a new range. Advantages are that clays can be very effective in both reducing penetration of water into the ground and removing lead from solution in water that does penetrate. Natural clay may suffice in some situations, minimizing costs. Even if an appropriate type of clay had to be brought to the site for construction of a suitable clay layer, costs would be relatively low in many cases. Disadvantages are that by minimizing infiltration, clay layers may increase surface runoff, and clay layers on the soil surface may not be optimal for support of vegetative cover to retard erosion.

4.6   ADDITION OF LIME

Dolomitic lime (agricultural lime or calcium carbonate) has been used to immobilize metals in soils by maintaining non-acid pH. Lime could be applied on the surface of the range as powder

using agricultural equipment, or could be spread as finely or coarsely crushed limestone for less

frequent applications. In addition to spreading on the soil surface, limestone could be beneficial

in some cases as part of structural control of runoff. Lining drainage ditches and settling ponds

with crushed limestone could help raise water pH, encouraging sorption of lead to soil particles

and reducing dissolved lead concentrations.

Liming of soils can also reduce plant uptake of lead under certain conditions. In laboratory

studies, the addition of lime to a variety of soils substantially reduced the uptake of lead in above

ground plant tissues of lettuce (*Lactuca sativa*), oats (*Avena sativa*), ryegrass (*Lolium* spp.), and

tobacco (*Nicotiana tabacum*) (Mench et al. 1994; John and Van Laerhoven 1972). Higher levels

of lead were observed in plant roots than plant shoots after liming, indicating that in these plants

without phytoextraction capabilities there is little translocation of lead from roots to shoots (John

and Van Laerhoven 1972). Although promising in laboratory studies, effects of liming on lead

mobility in field situations have not yet been proven. Lime has been used successfully as a

barrier for metals mobility for municipal solid waste leachate to surrounding soils (Bricka et al.

1993). However, since the solubility of metal hydroxides increases at both low and high pH,

lime should be applied (and periodically re-applied) as indicated by site-specific conditions.

Advantages of liming are that control of pH can be very effective in reducing lead solubility and

shifting lead from dissolved to particulate phases, which can be more easily controlled. Lime is

readily available in all parts of the country where soil acidity is an agricultural problem, is

inexpensive, and is easily applied with standard agricultural equipment. Disadvantages are that

it is of value only in areas with acid conditions, requires periodic replenishment and excessive

use can affect water quality in nearby water bodies. Powdered agricultural lime provides the

most intense effect, but requires the most frequent replenishment. Crushed limestone in

increasing particle sizes provided less intense effect but lasts longer. Optimal use of limestone

could require a mixture of powdered and crushed limestone applied at a rate determined by site-

specific conditions.

4.7   ADDITION OF PHOSPHATE ROCK

Commercially available finely ground phosphate rocks have been used as phosphate fertilizers

for years, especially in acid soils (Ma et al. 1995). Various forms of phosphate minerals have

been shown to immobilize lead in the environment (Nriagu 1974). Lead phosphates are the most

insoluble forms of lead in soils and can form rapidly in the presence of adequate lead and

available phosphate (Ma et al. 1995). Of the phosphate minerals, apatites are by far the most

abundant (Ma et al. 1993). Hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$] is effective for removing divalent

metal ions such as lead and has been used for wastewater treatment (Ma et al. 1994). Phosphate

rocks, with a composition approximating $Ca_{10}(PO_4)_6F_2$ have also been shown to immobilize lead

in water and soils (Ma et al. 1993, 1994, 1995). Phosphate rocks applied to lead-contaminated

soils reduced the water-soluble lead by 56.8 to 98.5% in some studies (Ma et al. 1993, 1995) and

showed similar lead immobilization capacity in the presence of other metals such as zinc, nickel,

copper, cadmium, aluminum, and iron (Ma et al. 1994). Immobilization of lead in soil by

phosphate rock addition did not require mixing to be effective (Ma et al. 1995). Immobilization

of lead was dependent on phosphate rock concentration, with increasing phosphate rock

decreasing the soluble lead (Ma et al. 1995). The decreased solubility of lead was achieved

under various conditions with a variety of soil and phosphate rock types (Ma et al. 1993, 1994,

1995).

In addition to immobilizing lead, these lead phosphate compounds are very insoluble, even in

the acidic environment of the human stomach (Ruby et al. 1994). This indicates limited

bioavailability to wildlife species under similar gastric conditions that incidentally ingest lead

while foraging on phosphate-treated ranges.

Advantages of phosphate additions are effectiveness and relative low cost. Except for

recover/recycle options, addition of finely ground phosphate rock to lead-contaminated soils may

provide the most cost-effective way of controlling lead mobility in soils at shooting ranges.

Disadvantages are that it is most effective under acid conditions, requires periodic replenishment

and excessive use can affect water quality in nearby water bodies. Powdered phosphate rock is

the most effective form, but requires the most frequent replenishment. Crushed phosphate rock

in increasing sizes lasts longer. Optimal use of phosphates would require a mixture of powdered

and crushed rock applied at a rate determined by site-specific range conditions.

4.8 ADDITION OF OTHER NATURAL OR SYNTHETIC MATERIALS

Although the additions of lime and phosphate rock are among the most frequently suggested

methods for reducing lead mobility in soils, other natural or synthetic additives could accomplish

the same purpose. Zeolite, a natural hydrated aluminosilicate crystal ($Na_2Al_2Si_4O_{12}$) has been

shown to remove metals from wastewater under full-scale applications (Bricka et al. 1993) and

reduce plant uptake of cadmium in soils (Mench et al. 1994). Zeolite is relatively stable across a

wide pH range (6-9), but should be applied only to neutral or alkaline soils or soils where the pH

is maintained in this range by liming (Bricka et al. 1993). Long-term effectiveness of zeolites for

controlling lead mobility at shooting ranges has not been established.

Beringite, a modified aluminosilicate mineral, can reduce or eliminate phytotoxicity of zinc and

cadmium in certain species of plants (Mench et al. 1994). Hydrous oxide constituents of

aluminum, iron, and manganese in soils have also been shown to reduce metals mobility in soils

(Mench et al. 1994). Any of these might prove useful for lead at ranges, but much more

investigation and documentation would be necessary before this could be determined. For any

such additives to be useful in control of lead mobility at ranges, it would be important that they

not produce any detrimental by-products or otherwise contribute to the environmental degradation of the site, and that their long-term effectiveness under field conditions be demonstrated.

4.9 SOIL CAPPING

Areas with bullets or shot may be covered or capped to reduce lead mobility (Heath et al. 1991). Covering impact berms or shot fields would involve capping with an impermeable layer of relatively uncontaminated topsoil and/or liner to collect future ammunition or shot. However, covering with additional soil may promote erosion and its effectiveness has not been field verified. As such, capping is not generally considered a long-term option for controlling lead mobility.

4.10 CULTIVATION/TILLING

Cultivation and tilling of soil at shotgun ranges have been shown to affect the weathering of lead shot (Jorgensen and Willems 1987). Shot in cultivated fields had six times as much "crust material" as shot from an adjacent uncultivated grassland, indicating more rapid weathering under cultivated field conditions (Jorgensen and Willems 1987). The crust materials consisted primarily of lead sulfate (anglesite) and the lead carbonate compounds hydrocerussite and

cerussite, which are some of the least water soluble lead compounds in oxidizing environments. However, their water solubility is considerably greater than metallic lead, and when combined with the physical alterations of the soil from cultivation (i.e., increased infiltration), result in increased mobility of lead in soils. Some tilling may be necessary to optimize plant growth (Sections 4.2 and 4.4), and tilling has been recommended to reduce the availability of shot to migrating birds. However, tilling can damage established vegetation and enhance the weathering of metallic lead into more soluble compounds. The use of tilling should be evaluated on a case-by-case basis.

4.11 COMBINED APPROACHES

Considering the spectrum of conditions found at shooting ranges across the United States, some ranges may not have any need to control lead mobility. At ranges where management of lead mobility may be appropriate, it is unlikely that all the preceeding techniques would be used. Some combination of these techniques tailored to address site-specific conditions is likely to be the most efficient and cost-effective approach.

The first step would be to determine whether lead mobility was a potential problem at the range in question, then to establish management objectives. If control were necessary, measurement of the factors controlling mobility at the site (e.g., pH, Eh, phosphates, sulfates, carbonates) would

provide the basis for determining which combination of management techniques would be most

appropriate. This information would also be necessary for establishing site-specific design

parameters (e.g., the amount and size of crushed limestone to provide optimum pH control).

5. ANALYTICAL CONSIDERATIONS FOR LEAD CONTAMINATED SITES

Various analytical and other test procedures have been used to assess potential lead mobility in environmental media. To accurately predict lead mobility, the test procedure must reasonably simulate conditions that control lead mobility in the field. Test procedures commonly employed by regulators and investigators (i.e., measuring concentrations of lead in water, sediment, and soil, and various leaching procedures) have attempted to address lead mobility with varying degrees of success. As discussed in Section 3, geochemical principles and experimental results demonstrate that lead is present in the environment in a variety of forms. Each chemical form has its own set of properties that greatly affect the fate and transport of lead. The interplay of these various forms will determine solubility, and thus mobility and bioavailability. Simply measuring the total quantity of lead present in water, sediment, or soil without considering additional parameters, or applying leaching procedures designed to address mobility in landfills will provide an inaccurate picture of the fate and transport of lead at shooting ranges. Because lead is readily precipitated and adsorbed, basing environmental risk or cleanup decisions only on total amounts of lead in soil or in a leaching procedure will, in general, grossly overestimate risk and result in unreasonable cleanup goals (Hem 1976, Rai et al. 1984, Ruggaber et al. 1990).

Section 5 describes the leaching and test procedures most likely to be applied to shooting

ranges, and discusses their technical strengths and limitations in accurately predicitng lead

mobility under typical conditions likely to be encountered at most ranges.

5.1 TOXICITY CHARACTERISTIC LEACHING PROCEDURE

The Toxicity Characteristic Leaching Procedure (TCLP) is an extraction procedure developed

by the U.S. EPA to determine whether a solid waste is classified as a hazardous waste (40

CFR 261.24) under the Resource Conservation and Recovery Act (RCRA). Solid wastes that

produce a lead concentration greater than 5.0 mg/L (5 ppm) in the TCLP leachate are

classified as hazardous.

The TCLP is designed to simulate conditions that typically occur in municipal landfills. The

premise behind the TCLP is that a typical municipal landfill contains a number of organic

materials that are degraded by bacteria, producing a number of weak organic acids. For this

reason, TCLP employs an acetic acid (0.1 N; pH 2.9)/acetate buffer (0.1 N; pH 4.9) solution

as a surrogate for municipal landfill leachate. Briefly, waste is agitated end-over-end in the

acetic acid/acetate buffer solution (20:1 leachate:waste ratio by weight) for 18 hours and the

resultant leachate solution analyzed for the chemical(s) of interest. If the resultant leachate

concentration exceeds the regulatory level (e.g., 5.0 mg/L for lead), the material is considered hazardous under RCRA.

In most cases, TCLP will greatly over-estimate the mobility of lead since the extraction procedure is conducted at low pH (≤ 5), and a variety of mechanisms that reduce lead-mobility in the environment (Section 3) are likely to be destroyed in a TCLP test. Because few shooting range soils or sediments are exposed to conditions prevailing in landfills as simulated by TCLP, it is not appropriate to use TCLP to estimate the mobility of lead at most shooting ranges. Even after removing lead for recycling purposes, shooting range soils may contain sufficient microparticulate lead to exceed the TCLP regulatory level of 5.0 mg/L.

5.2 STATE HAZARDOUS WASTE PROCEDURES

A number of states have developed their own procedures for classifying hazardous wastes (Heath et al. 1991). Some of the state procedures may be more or less severe than TCLP in terms of estimating leaching potential of wastes. For example, the State of California regulates hazardous wastes based on total chemical concentration and the Waste Extraction Test (WET). The California WET procedure uses a reduced leachate:waste ratio (10:1 vs. 20:1 for TCLP) and increased extraction period (48 hours vs. 18 hours for TCLP) that may increase or decrease the chemical (e.g., lead) concentration in the leachate solution and hence

could increase or decrease the chances of exceeding State regulatory levels. To the extent that state leaching procedures differ from conditions found at ranges in regard to factors controlling lead mobility, they are incapable of accurately predicting mobility in the actual environment.

5.3 SEDIMENT/SOIL ANALYSES

In many cases, the concentration of total lead is determined in sediment or soil samples to estimate lead mobility or bioavailability. Unfortunately, the total concentration of lead alone has little or no bearing on mobility or bioavailability. Other parameters such as pH, K_d (distribution coefficient), CEC, organic carbon, Fe-Mn oxides, redox conditions, acid volatile sulfide, carbonate, and phosphate (Section 3) may need to be considered in order to accurately characterize the mobility of lead (Hem 1976, Rai et al. 1984).

Simultaneously extracted metal/acid volatile sulfide (SEM/AVS) ratios are an effective method to demonstrate whether lead and other divalent metals in a reducing environment are available to sediment dwelling organisms (DiToro et al. 1990; Casas and Crecelius 1994). If lead sulfide is present, its log K_{sp} (solubility product coefficient) of <-33.4 precludes solubility in most cases (DiToro et al. 1990; Casas and Crecellus 1994). When the SEM/AVS ratio is below 1.0, toxicity of lead to benthic organisms is not expected because most of the lead is bound to sulfides and not bioavailable.

In conjunction with other parameters, total lead in soil can be important if modelling of potential groundwater contamination is appropriate. The CEC, organic carbon, Fe-Mn oxides, and pH can be used as inputs when estimating K_d values for modelling lead in groundwater under various conditions. The most appropriate parameters for this type of approach must be examined in a site-specific context. As shown in Section 3, several different approaches are operable under specific conditions. For this reason, site-specific conditions may indicate not only the necessary parameters but also the most appropriate K_d or speciation model.

If groundwater modelling is appropriate, case-specific experiments may prove the most expedient method of determining site-specific K or solubility values. In these experiments, it is most appropriate to use site water or nearby reference water to reflect the chemistry at the site, since many factors can affect the results. In this way, competition between ions, pH effects, and solubility-controlling species are all present at appropriate levels. Either of two types of experiments could be designed to obtain the necessary information: (1) a desorption experiment in which contaminated soils/sediments are placed in contact with relatively pristine water, or (2) an adsorption experiment where relatively uncontaminated soils/sediments are placed in contact with spiked reference water. The challenge in these experiments is maintaining site-specific conditions throughout the exposure period. Long contact times are often necessary in order to achieve equilibrium and it may be appropriate to collect a series of subsamples over time to determine when the experiment approaches equilibrium conditions.

5.4 WATER ANALYSES

Typically "total" lead is measured in whole water samples, as well as "dissolved" lead (filtered through a 0.45 μm filter). The dissolved lead in water most closely approximates the fraction biologically available to aquatic organisms (60 Federal Register 22228; 4 May 1995). Dissolved lead concentration is the value that should be compared to the U.S. EPA criterion for the protection of aquatic life in water quality evaluations.

The most reliable way to determine whether lead mobility in surface water at an operating or historic range might be an environmental problem is by direct analyses of surface water at the site. This could be standing or flowing water on the range, or nearby waterbody receiving runoff from the range. If a properly designed and conducted sampling program finds lead concentrations below the aquatic life and drinking water criteria, lead mobility in surface water is not likely to be a major environmental problem. If concentrations are above criteria, further investigation may be warranted.

Groundwater evaluation may be more complex, even if wells appropriate for sampling are available. Because contamination moves slowly in groundwater, data from a well taken at any point in time cannot indicate what the contamination in the well may be in the future. Therefore, the potential for groundwater contamination may best be evaluated by use of

appropriate groundwater models. These models require knowledge of total and dissolved lead, as well as K_d and other parameters. These total and dissolved lead values alone can be used as a means of measuring the K_d of lead, provided that suspended solids are present and were quantified. K_d can also be measured directly from the comparison of dissolved lead to total lead in sediment or soil. Since K_d is highly variable, samples should be paired with their corresponding soil/sediment in order to obtain accurate estimates.

If the goal is to identify a method of control dissolved lead concentration, it is usually necessary to use thermodynamic data coupled with site specific information. A number of additional chemical parameters not always determined in water or soil analyses may be important, including pH, sulfate, carbonate, phosphate, chloride, and sulfide. A limited knowledge of the site chemistry can be used to determine whether these factors should be quantified. The general stability field diagrams can be used as a guide Figures 3-1 and 3-3. For example, oxic sediments/soils are not likely to contain sulfide. Further, geochemical speciation modeling may preclude a solubility control if lead concentrations are below saturation levels and may point towards adsorption controls.

A further precautionary note is that water samples must be properly handled to ensure measurements are accurate. For example, carbonate tends to de-gas from samples,

acidification will increase dissolved levels of lead, and oxidation states may change on exposure of groundwater to atmospheric conditions.

5.5. SUMMARY

A number of analytical procedures used to estimate lead mobility and bioavailability in environmental media can be misleading. The TCLP leaching procedure is likely to overestimate lead mobility at most shooting ranges. Existing state leaching procedures may be more or less stringent that TCLP depending on the extraction procedure employed. The dissolved fraction of lead in surface water, rather than total concentrations, approximates the bioavailable fraction in most cases. Simple measurements of lead concentrations in soil and sediment do not provide an accurate assessment of lead bioavailability or mobility. Other factors such as acid volatile sulfide (AVS), CEC, pH, redox conditions, carbonate, and phosphate may play important roles in affecting lead mobility and bioavailability in sediments and soils. The simplest and most reliable indicator of lead mobility in surface water at existing or historical ranges is analysis of the water body in question. If detailed evaluation of mobility in groundwater is necessary, appropriate mathematical models may be useful.

6. CONCLUSIONS AND RECOMMENDATIONS

1. The environmental chemistry of metallic lead is sufficiently well known to understand the basic processes controlling lead mobility at outdoor shooting ranges.

2. Lead mobility at outdoor shooting ranges is not likely to be a serious environmental problem at most locations based on typical relationships of the major controlling variables.

3. Public and regulatory concerns about lead at outdoor ranges may be based on perceptions rather than full awareness and understanding of the scientific processes controlling lead mobility. However, it is possible that under unusual conditions that may occur at some ranges lead mobility could be of legitimate environmental concern.

4. Major influences on lead mobility are exerted by both extrinsic factors such as rainfall quantity and quality, and intrinsic factors like vegetative cover on the range. Intrinsic factors can be controlled to accommodate extrinsic factors in an environmental stewardship program to minimize lead mobility.

5. A variety of factors interact, perhaps in complex ways, to determine lead mobility.

6. The major chemical factors affecting lead mobility at outdoor shooting ranges are:

- pH

- precipitating agents (e.g., carbonates, sulfates, phosphates, sulfides)

- sorbents (e.g., iron and manganese oxides and hydroxides, organic carbon, clays)

7. Actual mobility at any particular range can only be determined only by appropriately designed site-specific evaluations at the range in question.

8. Some of the scientific literature on environmental chemistry of lead is limited by experimental design, poor detection limits, or analytical contamination. These do not affect the documentation of basic processes, but limit the utility of sorption coefficients and other chemical characteristics which are important for environmental fate and transport models.

9. Basic mechanisms determining lead mobility are sufficiently well known to identify promising control options for possible use at ranges where control might be appropriate.

10. Promising options to control lead mobility at ranges include lead recovery/recycling, control of runoff, additions of agricultural lime or phosphate, and clay layers.

However, the effectiveness of these options has yet to be demonstrated in practice with sufficient detail to provide the technical basis for site-specific design and implementation.

11. Optimum control might require a combination of options selected and applied in response to site-specific conditions.

12. The TCLP and other leaching tests were not designed to simulate conditions at shooting ranges and are not technically appropriate for predicting lead mobility at ranges.

13. The critical values for the major controlling factors (e.g., how much soil phosphate is sufficient to effectively limit lead mobility) have not been adequately documented in relation to conditions found at ranges.

14. The interactions of different controlling factors (e.g., the influence of soil organic matter on the tendency toward higher mobility at lower pHs) can be generally hypothesized, but has not been adequately documented based on controlled laboratory studies.

15. Management of lead mobility at ranges might be improved with a better understanding of

real-world conditions affecting:

· interactions among controlling factors.

· critical values for major controlling factors.

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